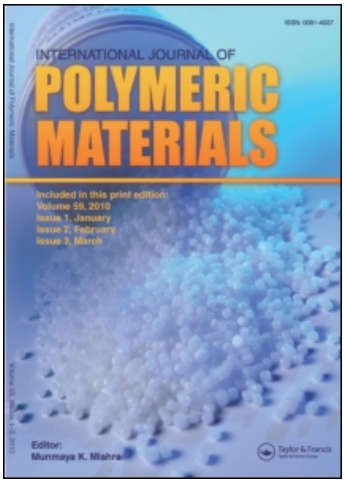

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PROPERTIES OF PAPER SHEETS PREPARED FROM *IN-SITU* SYNTHESIS OF CUPRITE IN WOOD PULP FIBERS

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Wood pulp-cuprite paper sheets were prepared from in-situ synthesis of copper(I)-oxide in wood pulp fibers, to study its effect on fire retardant property. Factors such as the amount of copper sulfate, amount of reducing carbohydrate, pH-value, temperature and the amount of carboxymethyl cellulose were studied to derive the optimum conditions for the formation of Cu(I)O with maintaining or improving the strength properties of the prepared paper sheets. The X-ray diffraction was used to identify the formation of Cu(I)O inside the fibers; while FTIR-spectroscopy analysis was used to clarify the behaviour of Cu(I)O inside the fibers.

The electrical properties of the prepared paper sheets, e.g., AC-conductivity (σ), dielectric constant (ε') and dielectric loss (ε'') were also examined. The thermal degradation behaviour of some prepared paper sheets has been studied by means of non-isothermal thermogravimetric analysis, and the kinetic parameters were estimated by using Coats and Redfern equation. The results obtained show a good relation between the amount of formed cuprite with the mechanical and electrical properties of the produced sheets. The formation of cuprite in wood pulp fibers improves the fire retardants property of the paper sheets; while the addition of CMC during cuprite formation diminishes this effect.

Keywords: cuprite, wood pulp fibers, synthesis, properties

INTRODUCTION

The field of metal-containing polymeric materials has received much attention during the last two decades because of the burgeoining interest in the search for new high performance materials [1–5], especially in the electric field, *e.g.*, the formation of composite metallopolymeric coatings

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both on steel and on copper [6]. This type of materials was prepared either by introducing the metal ions by chelation through functional groups in the polymers [7–12], or by blending the polymers with oxides [13–16].

In the literature there are reports of the use of metal oxides in the preparation of semiconducting ferrites [17], and as paper additives to improve optical and printing properties (*e.g.*, TiO_2), or to improve the magnetic property, *e.g.*, Fe_2O_3 [18, 19]. The polycrystalline semiconductor oxides (*e.g.*, ZnO and TiO_2) can enhance the bleaching effect of spruce wood pulp by using oxygen [20]. The Cu_2O, MoO_3 and Sb_2O_3 are used as a smoke retarder additives function in PVC [21, 22].

This study has been carried out to examine the influence of *in-situ* formation of cuprite in wood pulp fibers, purposing to improve the fire retardency property, on the mechanical and electrical properties of the prepared paper sheets. The thermal analysis technique was used to follow the fire retardency behaviour of the prepared wood pulp-cuprite paper sheets, which regards the main objective of this study.

EXPERIMENTAL

Materials

- Paper-grade wood pulp provided by RAKTA-Paper Mill, Alexandria, Egypt was used as the paper stock. This pulp was chemically analysed for (α-cellulose [23], pentosans [24], lignin [25] and ash content.
- High chemical grades of copper sulfate, citric acid, sodium hydroxide, sodium carbonate, glucose and carboxymethyl cellulose (CMC, D.S. 0.7).

Preparation of Paper Sheets Containing Cuprite and Its Mechanical Measurements

A calculated amount of copper sulfate (10%/pulp) was added to pre-beaten wood pulp (43°SR) with a solution containing a mixture of citric acid, sodium hydroxide and sodium carbonate in ratio 7.4 : 4.7 : 5.8 (based on $CuSO_4$) in addition to 40% (based also on pulp) glucose, at pH $\sim$ 7.7. The resulting mixture was left 0.5 hour at 60°C. This step was carried out in sealed polyethylene bag with different formation variables, such as $CuSO_4$ (2–20%/pulp), glucose (20–80%/pulp), temperature (60–100°C), CMC (2–10%/pulp), and pH of sheet formation (9.3–4.4).

The paper sheets either from untreated or wood pulp treated fibers were prepared according to the Swedish Standard method. The paper hand-sheets were placed for conditioning at relative humidity of 65% and a temperature of 18–20°C, then they were tested for breaking length, burst and tear factors [26]. The ash content of the prepared sheets was also estimated as an indication to the percentage of cuprite in paper samples.

Other Measurements

X-ray Diffraction Analysis

The patterns for identification of the formed cuprite by X-ray analysis were run on a Siemens D-500 using CoKα-radiation ($\lambda = 1.79$). The X-ray tube was energized at 35 k.v. and 15 mA. The 2θ was scanned at 2°/minute, and the chart speed at 1 cm/minute. Identification of the different phases was carried out by measuring the diffraction angle and, accordingly, the corresponding d-values in Ångstrom. JCPDS card was used for evaluation.

FTIR-Spectra

IR-spectra ($4000 - 200\,cm^{-1}$) were recorded on an Insco FT/IR-Infra red spectrophotometer using KBr disc.

Electrical Properties

An LCR meter type AG-U11B Ando Electric LTD Japan was used to measure the dielectric parameters in the frequency range between 100 Hz and 50 kHz. The capacitance (C), loss tangent ($\tan\delta$) and A.C. resistance (R) were measured directly from the bridge, from which dielectric constant (ε'), dielectric loss (ε''), and σ_{AC} were calculated.

A guard ring capacitor type NFM/5T from Wiss Tech. Werkstatten (WTW) GMBH, Germany was used as a measuring cell. The cell was calibrated using standard materials with known permittivities [ε' (air) = 1, ε' (tralitul) = 2.54 and ε' (glass) = 7] [27]. The experimental error in ε' was $\pm 3\%$; in ε'', $\pm 5\%$. All the measured paper samples have a thickness of 1 mm and nearly the same moisture content $\sim 3.2\%$.

Thermal Analysis

Thermogravimetric analyses (TG and DTG) of the prepared paper sheets including different amount of the formed cuprite were done using PERKIN ELIMER (Thermo-gravimetric Analyzer TGA 7). Analysis was performed with a heating rate 10°/minute and flow rate 50 cc/minute, under non-isothermal conditions, in the presence of nitrogen.

RESULTS AND DISCUSSION

Table 1 represents the chemical constituents of the wood pulp used as a paper stock and the properties of handsheets made from it, without treatment.

Identification of the Formed Oxide by X-ray Analysis

The X-ray diffraction patterns of the formed cuprite, without pulp, and paper sheets prepared from both untreated and cuprite-wood pulp (sheets

TABLE 1 Chemical analysis of wood pulp and mechanical properties of its paper sheets

Property	*Value*
α-Cellulose, %	89.5
Pentosans,%	8.7
Lignin, %	Trace
Ash, %	0.212
Breaking length, m	3540.12
Burst factor	33.400
Tear factor	138.388

formation at different pH's; 4.4, 7.7 and 9.3), are clear in Figure 1. The interplaner spacing (d's) of the formed oxide confirm the formation of cuprite [Cu(I)O]. Also, it is clear that the pH's of the sheet formation plays an important effect on the stability of the formed cuprite. Whereas, at pH 4.4 the formation of cuprite inside wood fibers is less probable than alkaline pH's (7.7 and 9.3).

Mechanical Properties

In order to compare the change in the mechanical properties of the prepared paper sheets as a function of the examined variables, a ratio "R" was developed, which is represented as follows:

$$\text{Relative change } (R) = \frac{\text{reading value}}{\text{initial value}}$$

where, initial value is the mechanical properties of the paper sheets prepared from untreated wood pulp.

The relative changes (R's) in the mechanical properties of paper sheets prepared from *in-situ* formation of cuprite in pulp fibre as a function of the amount of $CuSO_4$, amount of glucose, temperature, pH value or amount of CMC are illustrared in Figures 2–4.

For the effect of the percentage of $CuSO_4$ (Fig. 2a) it is clear that the formed cuprite gradually increased with increasing percentage of $CuSO_4$ from 2% to 20% (based on wt. of wood pulp); while the greatest improvement in strength properties is noticed on adding 8% $CuSO_4$. A further increase in the added amount of $CuSO_4$ caused a reduction in the strength properties of the paper sheets obtained.

For the effect of the amount of added glucose, Figure 2b shows that the improvement in the strength properties increased with the increase of

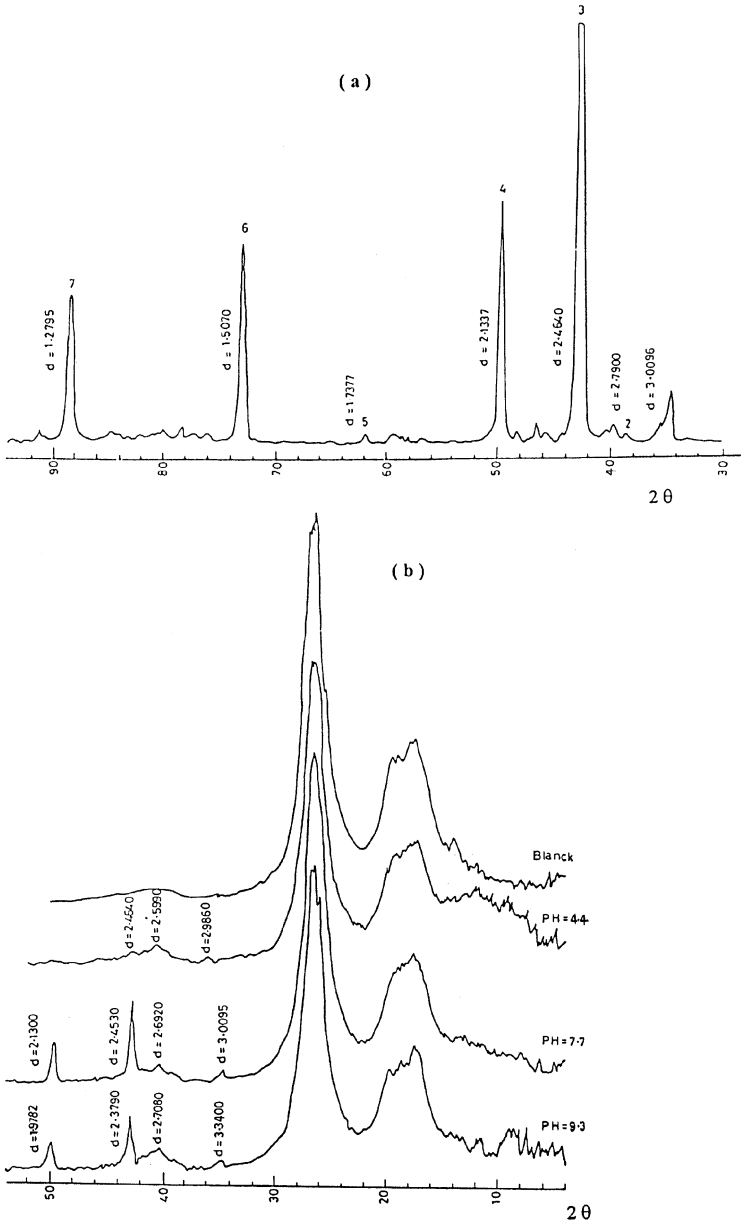

FIGURE 1 X-ray diffraction patterns of (a) formed oxide and (b) untreated and treated paper samples.

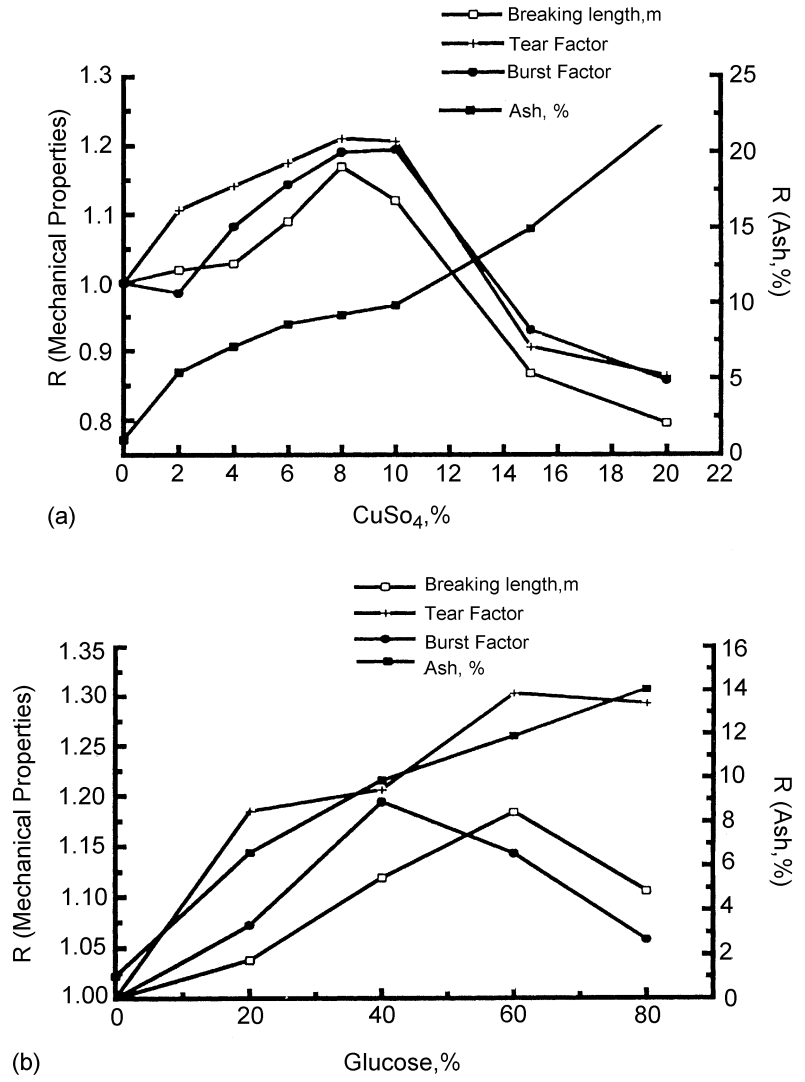

FIGURE 2 Effect of $CuSO_4$ and glucose percentages on the relative changes, R (based on untreated paper sheet) of mechanical properties and ash contents of treated paper sheets.

glucose percentage which was added as a reducing carbohydrate to copper sulfate. Maximum improvement is noticed at 60% glucose (based on wt. of pulp). As the case of the effect of $CuSO_4$ percentage, increasing the percent of glucose leads to an increase in the ash content of paper sheets, *i.e.*, the

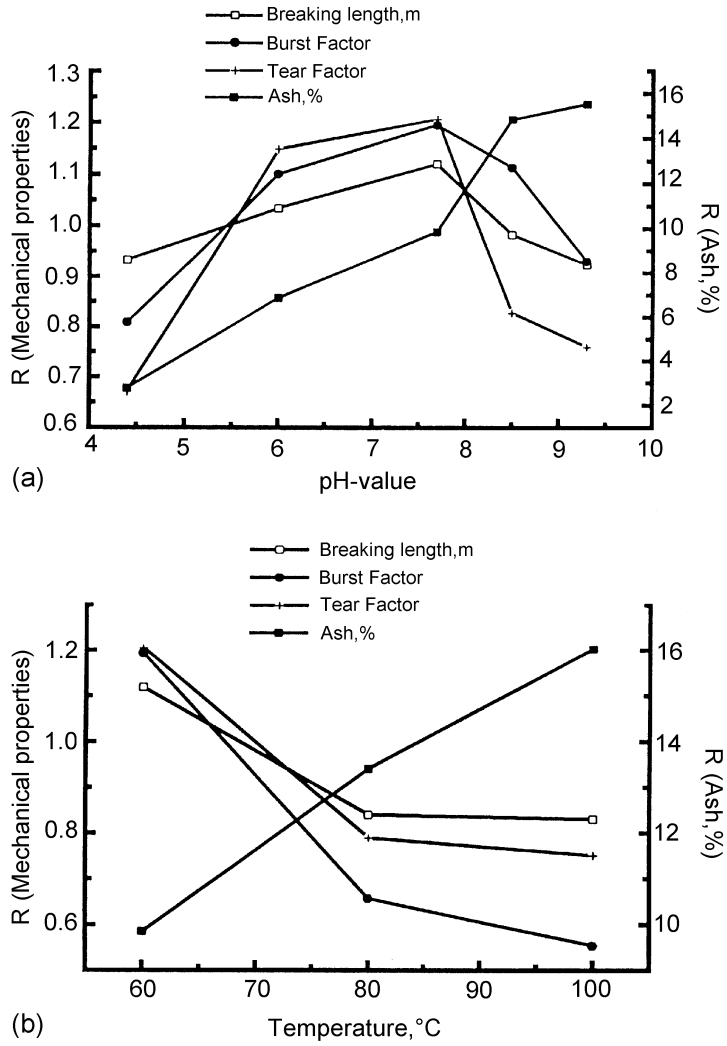

FIGURE 3 Effect of pH-value and temperature on the relative changes, *R* (based on untreated paper sheet) of mechanical properties and ash contents of treated paper sheets.

amount of formed cuprite, but to a lower extent than the change in $CuSO_4$ percentage.

For the effect of temperature during cuprite formation inside pulp fibres (Fig. 3b) it is clear that although the increase of temperature from 60°C to

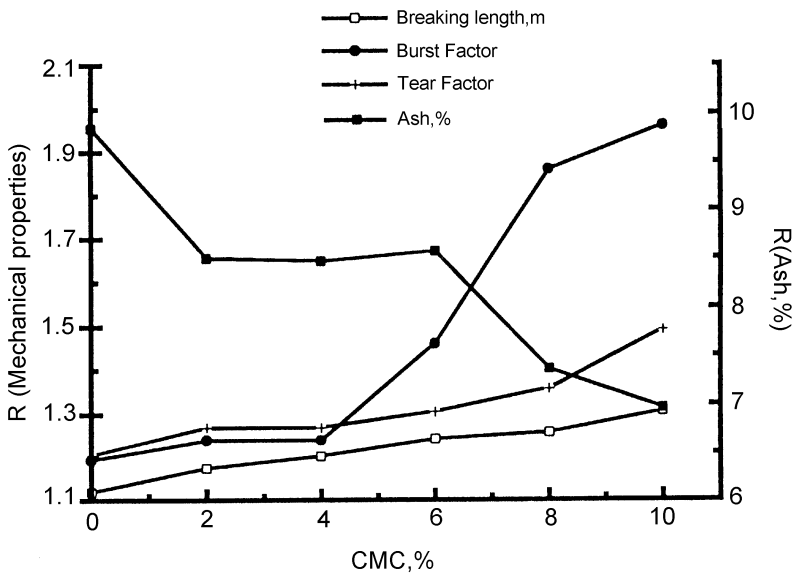

FIGURE 4 Effect of carboxymethyl cellulose percentage on the relative changes, *R* (based on untreated paper sheet) of mechanical properties and ash contents of treated paper sheets.

100°C leads to an increase in the formed cuprite, the relative changes in the mechanical properties were negative (*i.e.*, deterirated).

For the change in the pH value of cuprite wood pulp suspension from 7.7 to 4.35, 6.0, 8.5 or 9.3 by using dilute HCl or NaOH, Figure 3a shows that increasing or lowering the pH value than 7.7 both deteriorate the mechanical properties of the obtained sheets. Elevating the pH-value to 8.5–9.3 leads to an increase the percentage of ash, this is probably related to the precipitation of the formed cuprite as copper hydroxide when alkali was added to the suspension. On reducing the pH from 7.7 to 4.4, most of cuprite was converted to copper chloride which was probably lost during sheet formation, this view was emphasized from X-ray diffraction patterns (Fig. 1b).

As shown in Figure 4, the relative change in the strength properties of paper sheets, as a result of changing the percent of the added CMC were improved gradually on increasing the amount of CMC from 2% to 10% (based on pulp); while the reverse trend is noticed in the case of ash content. This may be attributed to the competition between the CMC and reducing carbohydrate (glucose) to react with copper sulfate either to form CMC–Cu(II) complex or cuprite. At relatively high CMC per cents (8–10%), the

probability of CMC to chelate with Cu(II) ions is higher than the reduction of $CuSO_4$ to Cu(I)O by glucose.

To clarify the behavior of cuprite inside the pulp fibers, especially for improving the strength properties of sheets obtained, the FTIR-spectra of some prepared sheets having different ash contents and relatively high strength properties were recorded. The examined paper samples are:

(1) Paper sheet from untreated wood pulp,
(2) Paper sheet prepared from wood pulp-cuprite fibers. The conditions of cuprite formation are: $CuSO_4$ 10%, glucose 20% and pH 7.7 for 0.5 hr. at 60°C. The other chemicals (citric acid, NaOH and Na_2CO_3) are constant as in the experimental section,
(3) The same as Sample 2, but the amount of glucose 60% instead of 20%,
(4) The same as Sample 2, but the amount of glucose 40% with adding 10% CMC, and
(5) The same as Sample 2, but the amount of glucose 40% and pH of sheet formation is 4.35.

The percentages of ash content are 0.21, 1.397, 2.52, 1.48 and 0.59, respectively. Tables 2 shows the IR-frequency bands and mean hydrogen bond strength [28], of the examined paper samples. It is clear that, the characteristic stretching bands of hydroxyl and carbonyl groups shifted

TABLE 2 IR-frequency bands, $\nu\,cm^{-1}$, and mean hydrogen bond strength of some examined paper samples

Sample no.	1	2	3	4	5
IR-frequencies cm^{-1}	3421	3414	3406	3419	3397
	2902	2902	2902	2902	2902
	1655	1637	1637	1637	1655
	1430	1430	1430	1430	1430
	1375	1375	1375	1375	1373
	1320	1320	1320	1320	1320
	1165	1165	1165	1165	1165
	115	1115	1115	1115	1115
	1058	1058	1059	1058	1059
	900	900	900	900	900
	617	617	617	617	617
	–	351	350	–	–
	235	233.3	235	235	237
	220	218	218	220	218
	–	–	–	204	–
MHBS $A_{OH\ (str.)}/A_{CH\ (str.)}$	1.4034	1.4524	1.5072	1.573	1.6105

from 3421 cm^{-1} to 3414 cm^{-1} and from 1655 cm^{-1} to 1637.3 cm^{-1} for the sheet including cuprite with ash content 1.397% (Sample 2), compared with paper Sample 1. The extent of the shift of the band maximum of OH-stretching increased with increasing the ash percentage to 2.52 (Amax. at 3406 cm^{-1}, Sample 3); while no change in the position of C=O was noticed. Also, a new band appeared in the region of 200–400 cm^{-1}, this band confirmed the presence of Cu—O [29].

The shift of the OH band may be related to the oxidation of some hydroxyl groups by Cu(I)O, and consequently the degree of hydrogen bonding increased. In other words, the formation of cuprite in wood pulp fibers leads to destruction of the weak hydrogen bonds by oxidation and subsequent re-ordering of the chains, with the formation of new and stronger hydrogen bonds. Badger and Bauer found that the value of the shift in the stretching vibration of OH groups is a measure of the strength of hydrogen bonds [30]. Therefore, the improvement in the strength properties of the wood pulp-cuprite sheets of Sample 3 is relatively higher than Sample 2.

The above view (oxidation and re-ordering of hydroxyl groups) is supported by decreases in the strength of paper sheets on adjusting the pH during cuprite formed in wood fibers to 4.4 (Sample 5), compared with wood pulp-cuprite sheet at pH 7.7 (Sample 3), Figure 3a. Where in the former sample no cuprite is formed under alkaline conditions; while the red shift of the band assigned to stretching vibration of OH groups with the increase in the ash content, with respect to untreated sheets, may be related to absorption behaviour of hydroxyl group to copper ions, *i.e.*, OH groups are bonded by Cu(II) ions.

However, the observed improvement in strength properties of sheets including relatively low cuprite (ash, % < 2.1–2.5) compared to higher cuprite (Fig. 2a) is probably related to the regular distribution of the small amount of formed cuprite within the fibers. At high levels, cuprite between the fibres weaken and dissipates the interfiber bonding, so the paper loses its strength.

The appearance of a red shift in the band maxima correspond to C=O groups of spectra Samples 2–3 (Tab. 2) indicates that carbonyl groups are shared in cuprite-wood pulp composite.

For the case of adding CMC during the cuprite formation (Sample 4, Tab. 2), the characteristic stretching of the carbonyl group also shifted from 1655 cm^{-1} to 1637 cm^{-1}. This may be due to the chelation of Cu(II) ions through carboxylate group of CMC.

Electrical Properties

Figures 5–9 show the variation of dielectric constant (ε') concomitant with the dielectric loss (ε'') as a function of log frequency ($\sim$25°C) for all

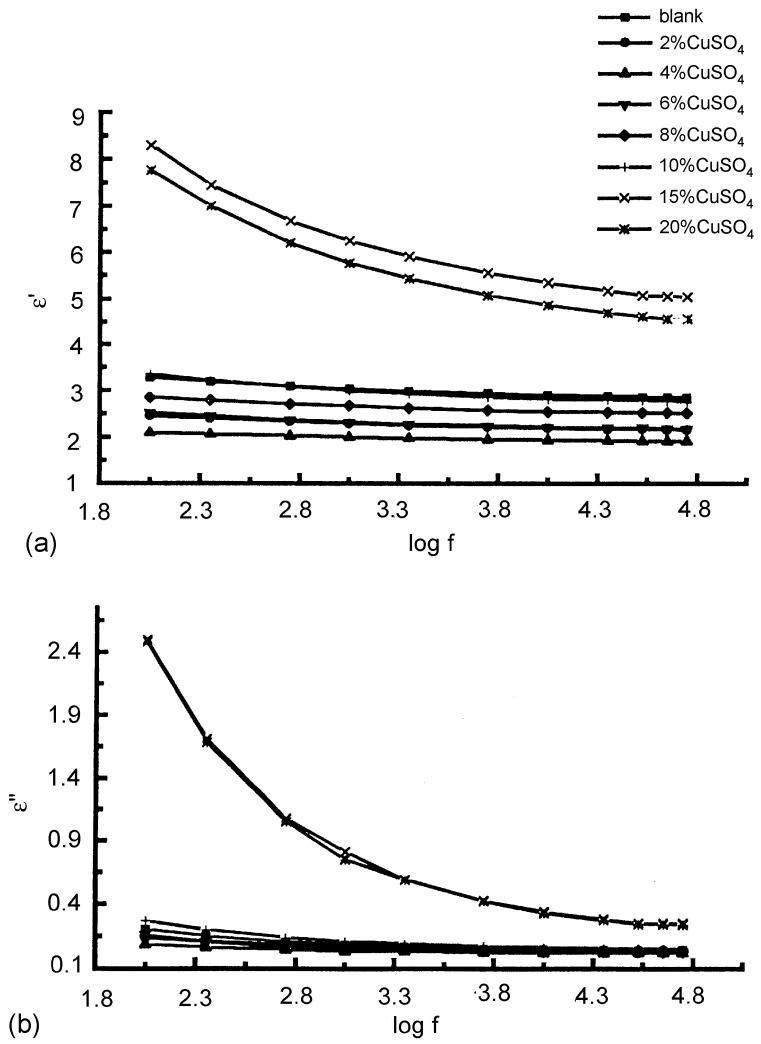

FIGURE 5 Variation of dielectric constant (ε') and dielectric loss (ε'') with frequencies of paper sheets obtained at different $CuSO_4$, % (during formation of cuprite).

pre-tested paper samples; while Figures 10–14 show the variation of ε', ε'' (at 2 kHz) and AC-conductivity (at 15 kHz) as a function of ash content of the paper sheets obtained from the effect of the examined variables.

It is evident from Figures 5–9 that, generally the dielectric constant and dielectric loss decreased with increasing frequency from 0.1 to 50 kHz. This

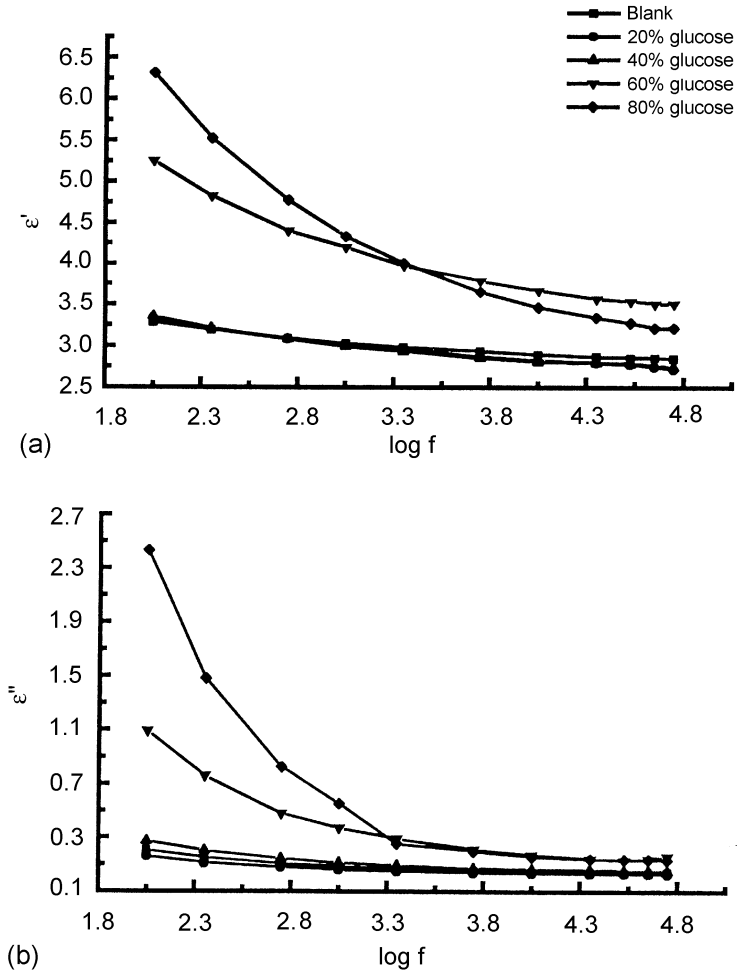

FIGURE 6 Variation of dielectric constant (ε') and dielectric loss (ε'') with frequencies of paper sheets obtained at different glucose, % (during formation of cuprite).

decrease can be attributed to the dielectric dispersion occuring with the increased frequency, which results from the lag of the molecules behind the cycle of the applied electric field [31].

From Figures 10–14 it is also clear that, generally there is a good relationship between the percentage of ash content (cuprite formation) and dielectric properties (σ_{AC}, ε' and ε'') of paper sheets. This is related to the increase in the amount of formed cuprite which has relatively high electrical properties than wood pulp fibers, as clear in Table 3.

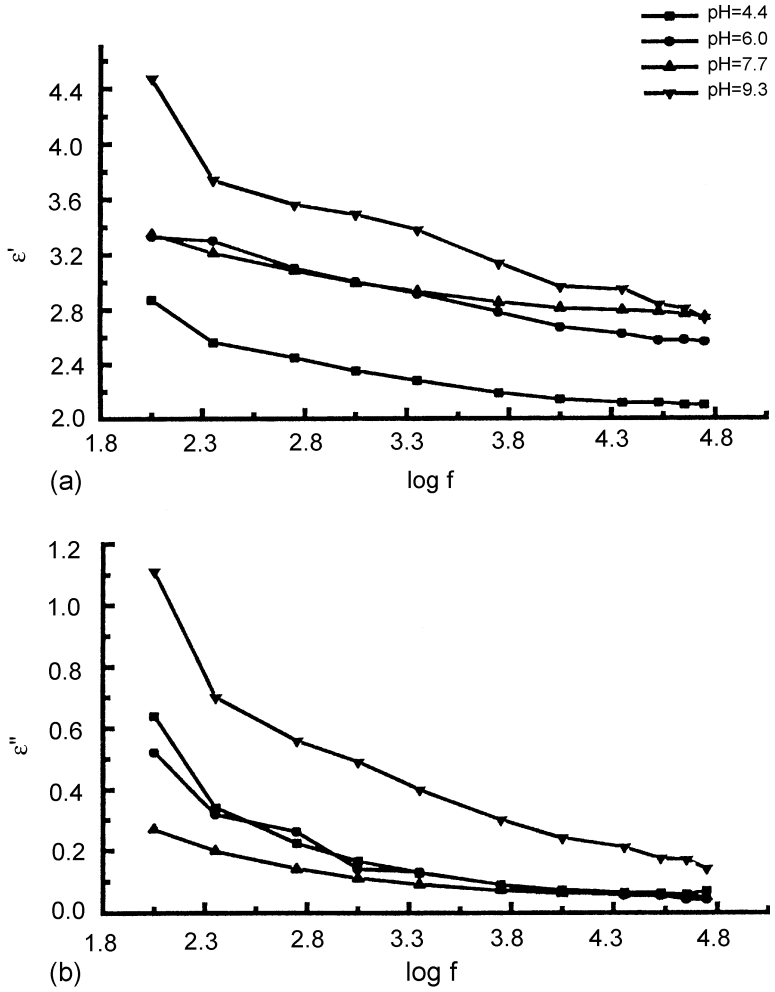

FIGURE 7 Variation of dielectric constant (ε') and dielectric loss (ε'') with frequencies of paper sheets obtained at different pH's (during formation of cuprite).

In order to explain the observed increase in the electrical properties of sheets, as a result of *in-situ* synthesis of cuprite in wood pulp fibers, the electrical properties of the cuprite powder and the paper sheet made from untreated wood pulp were compared, Table 3 shows the higher electrical properties of cuprite than wood pulp sheet.

However, the relative decrease in the electrical constant ($\varepsilon' = 2.2$, Fig. 13) of sheets formed at pH $\sim$ 4.4 compared to that value of untreated sheets

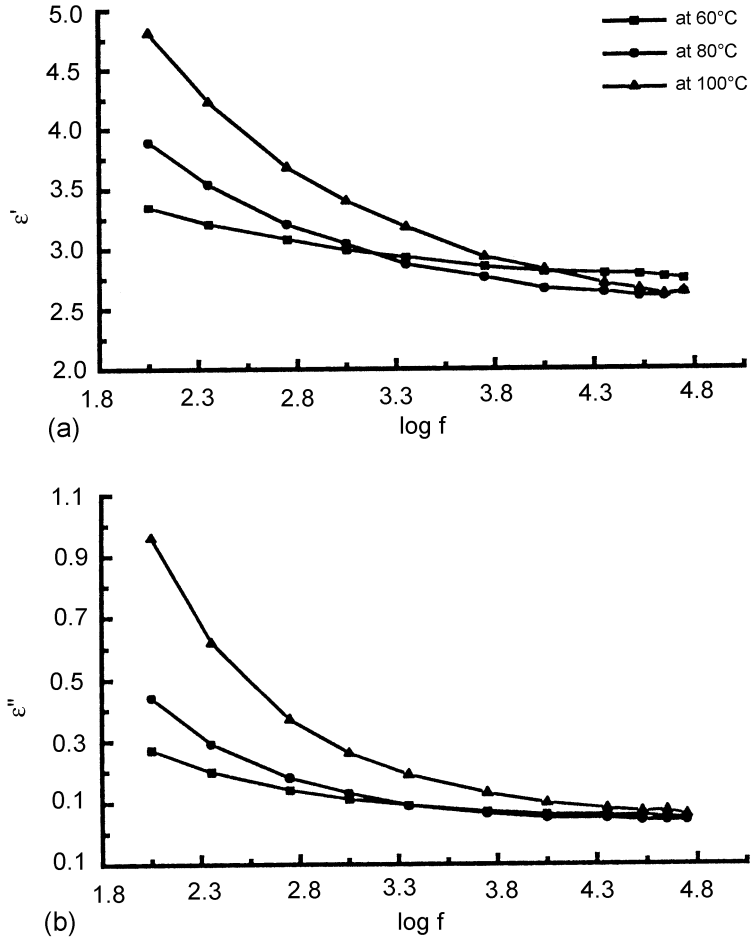

FIGURE 8 Variation of dielectric constant (ε') and dielectric loss (ε'') with frequencies of paper sheets obtained at different temperatures (during formation of cuprite).

($\varepsilon' = 3$, Fig. 10) is related to reduced number of free hydroxyl groups in the former case by binding them with Cu(II) ions, as shown from the measurements of the mean hydrogen bond strength, MHBS, Table 2, and the greatest shift of the band maximum correspond to stretching vibration of OH groups to lower wave number ($\Delta\nu = 24$); Table 2. The dielectric properties of cellulose sample depend on the number of free OH groups [32].

From Figures 5 and 14 it is clear that, the addition of a relatively high percentage of CMC (10%/pulp) during cuprite formation decreases the ash

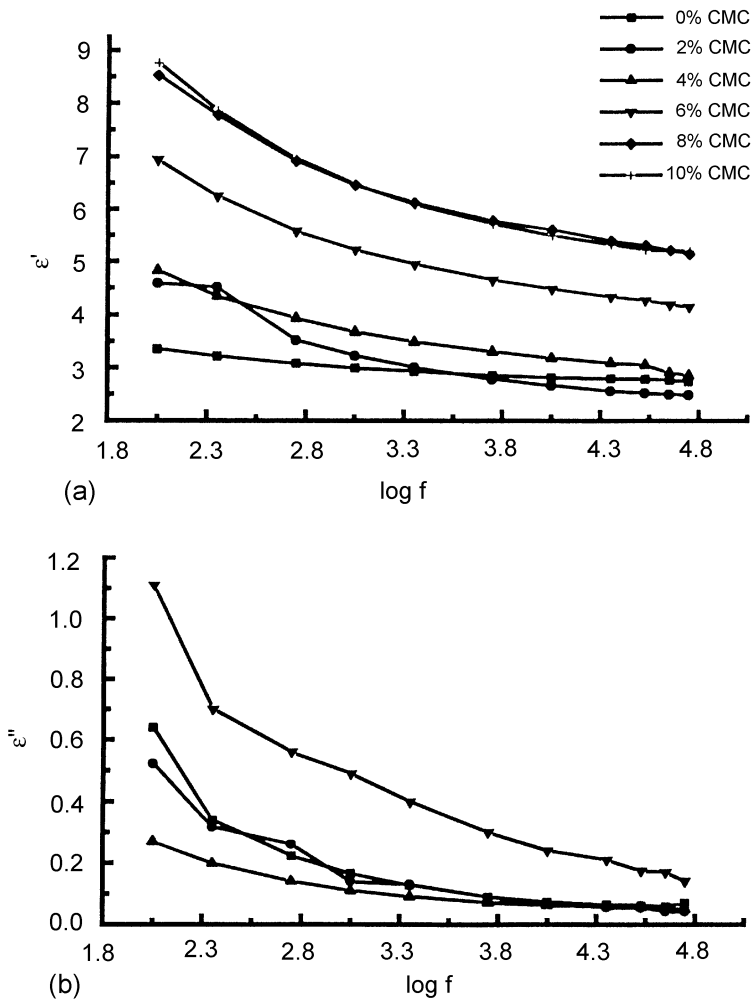

FIGURE 9 Variation of dielectric constant (ε') and dielectric loss (ε'') with frequencies of paper sheets obtained at different CMC, % (during formation of cuprite).

content of the paper sheet obtained, and at the same time increases the electrical measurements (ε', ε'' and σ_{AC}). This may be related to an increase in the probability of reaction between CMC and Cu(II) ions with the formation of CMC–Cu(II) complex compared the reduction of $CuSO_4$ to Cu(I)O by glucose. In other words, the proposed changes take place in weakly hydrogen-bonded region of cellulose chains by oxidation of OH due to the formation of Cu(I)O, followed by reordering of the chains with the

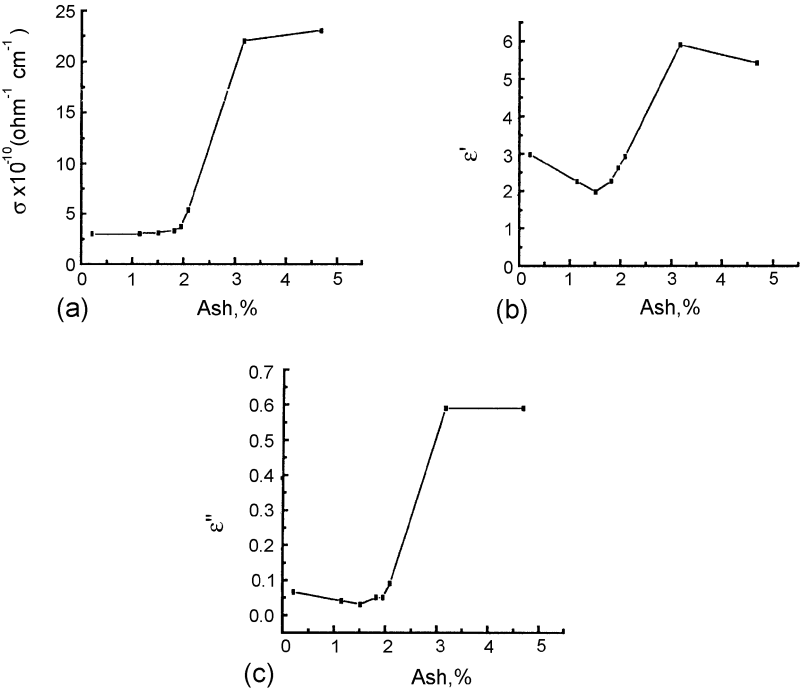

FIGURE 10 Relation between (at 15 kHz) and ε' and ε'' (at 2 kHz) *vs.* ash content of paper sheets produced from changing the $CuSO_4$, % during cuprite formation.

formation of stronger hydrogen bonds is prevented at relatively high CMC addition. The formation of CMC–Cu(II) complex creates inter-chain spaces [33]. This inter-spaces may enhance the mobility and ionization of the OH groups in accessible regions of cellulosic materials. Therefore, the increase in the electrical properties is mainly related to the amount of cuprite formed and micropores in the fiber chains.

In the light of the above results, the high mechanical and agreeable dielectric properties of wood pulp-cuprite samples, made from adding 60% glucose as reducing agent of $CuSO_4$ or adding 40% glucose and 10% CMC, can be used in industrial application as electrical paper [34, 35].

Thermal Properties

The non-isothermal TG and DTG curves of the paper sheets examined by FTIR (Samples 1–4), having different ash contents (0.21–2.52%), are illustrated in Figure 15.

The determination of kinetic parameters (activation energy, E_a, and frequency factor, A) from weight loss *versus* temperature data can be carried

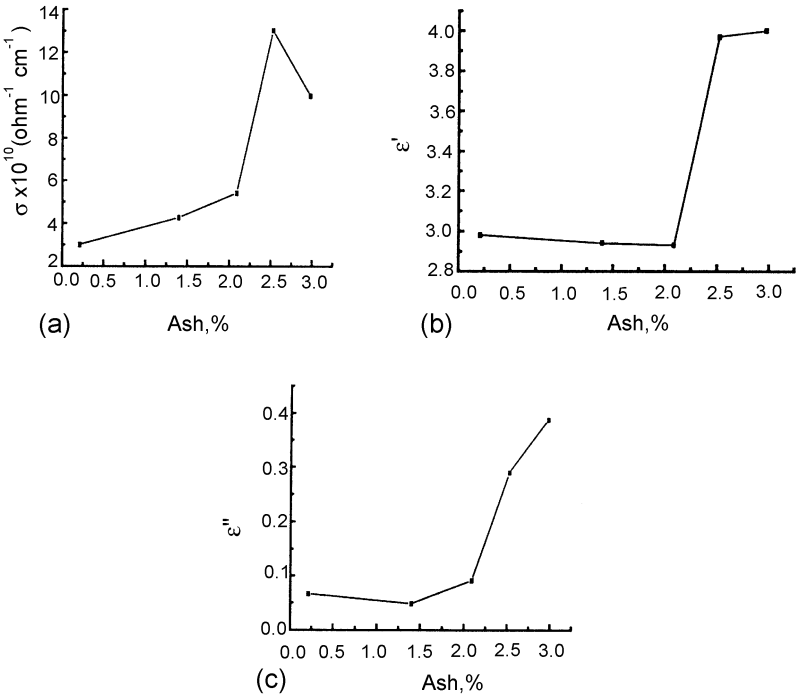

FIGURE 11 Relation between (at 15 kHz) and ε' and ε'' (at 2 kHz) *vs.* ash content of paper sheets produced from changing the glucose, % during cuprite formation.

out by using Coats and Redfern equation [36]. The general correlation equation used is

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log_{10}\left[\frac{AR}{aE_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{2.3RT}$$

where α is the fractional conversion, n is the order of reaction, a is the heating rate (in $\mathrm{K\,min^{-1}}$), R is the gas constant (in $\mathrm{kJ\,mol^{-1}\,K^{-1}}$) and T is the temperature (in K) and A is the frequency factor ($\mathrm{s^{-1}}$).

Plotting the left-hand-side values of the equation, *i.e.*, $\log_{10}[1-(1-\alpha)^{1-n}/T^2(1-n)]$ against $1/T$ using different values of n, should give a straight line with the most appropriate value [37]. Thus, the method of least square is applied for the equation, taking values of n ranging from zero to 3.0 with increment of 0.5, and calculating for each value of n, the correlation coefficient, $-r$, and standard error estimation, SE. The n values which corresponds to the maximum, $-r$, and minimum, SE, is the order of the

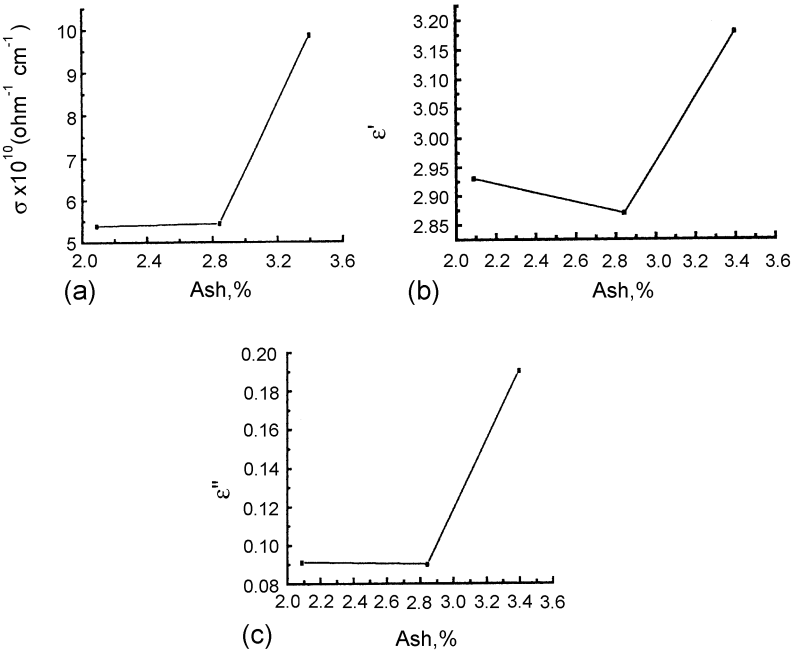

FIGURE 12 Relation between (at 15 kHz) and ε' and ε'' (at 2 kHz) *vs.* ash content of paper sheets produced from changing the temperature during cuprite formation.

degradation process. The E_a and A were calculated from the slope and intercept, respectively. Figure 16 represents the plot of $-r$ and SE as a function of n, for the decomposition stages of untreated wood pulp paper sheet to calculate the appropriate order of degradation.

Table 4 summarize the temperature range, $-r$, SE, n, E_a, A and k for two main degradation stages of the investigated paper samples.

From Figure 15 it is clear that, in all paper samples, three degradation stages are observed. The first stage at temperature $< 100°C$ this is due to the loss of the sorbed moisture; while in temperature region 203 – 349°C, the degradation is due to the following reactions : hydrolysis of glucosidic bonds (depolymerization), thermo-oxidation and dehydration. This range incorporates the temperatures used in the preparation of levoglucosans and related products obtained by the pyrolysis of cellulose [38, 39]. At higher temperature ($> 361°C$) the degradation stages is due to rapid volatilization accompanied by the formation of carbonaceous residue.

From Table 4 it is clear that, the decomposition temperature of the paper samples including relatively low ash content (Samples 2 and 4; ash

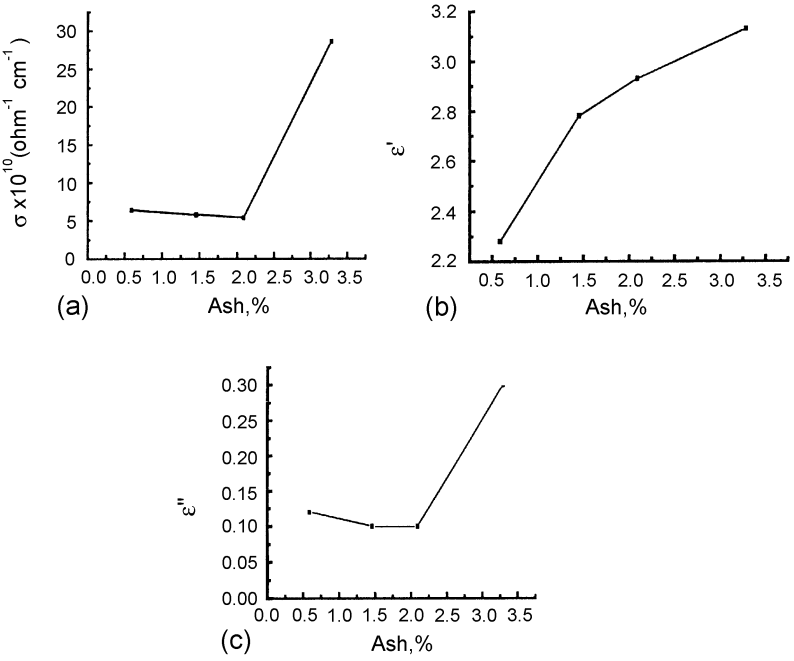

FIGURE 13 Relation between (at 15 kHz) and ε' and ε'' (at 2 kHz) *vs.* ash content of paper sheets produced from changing the pH during paper sheet formation.

% 1.397 and 1.48, respectively) is higher than untreated sheets, however, the reverse trend is observed in the case of relatively high cuprite formation (Sample 3; ash % 2.52). In other words, the onset temperature for weight loss is found to have been lowered by *in-situ* formation of cuprite in paper sheet with ash content 2.52% The relatively increase in the E_a of Sample 4 compared to that of Sample 2, despite them having nearly equal percentages of cuprite, may be related to the strength properties of the sheets obtained (Figs. 2b and 5)

The values of DTG peaks (Fig. 15b) and the specific rate constants (Tab. 4) of the degradation stages corresponding to the creation of levoglucosans (1st main degradation stages), show that the relatively high *in-situ* formation of cuprite (2.52% ash content; Sample 3) increases the rate of depolymerization and dehydration, *i.e.*, decreases the formation of levoglucosans which is regarded as the main source of fuel for a flame [40]. Therefore, such treatment reduces the flammability of paper sheets. The fire retardancy property of the sheets obtained is expected to increase with increasing the cuprite formed in pulp fibers of ash content over 2.52%.

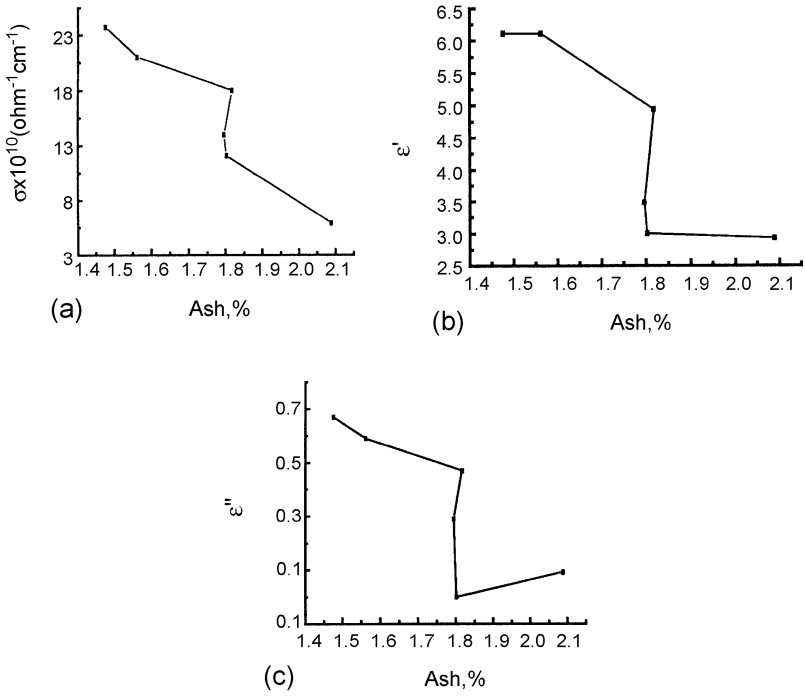

FIGURE 14 Relation between (at 15 kHz) and ε' and ε'' (at 2 kHz) *vs.* ash content of paper sheets produced from changing the CMC, % during cuprite formation.

TABLE 3 Electrical measurements of cuprite and paper sheet made from untreated wood pulp

Sample	ε' (2 *kHz*)	ε'' (2 *kHz*)	$\sigma\ (\Omega^{-1}\,cm^{-1})$ *at* 15 *kHz*
Cuprite	29.310	10.550	4.938×10^{-8}
Untreated paper sheets	2.979	0.066	3.000×10^{-10}

From all the foregoing results it can be concluded that,

– The optimum conditions for increasing the percentage of formed cuprite in pulp fibers (Ash, % 2.52) to improve the strength properties are: 10% $CuSO_4$, 60% glucose and pH 7.7 for 0.5 hr. at 60°C. The effect of adding CMC plus glucose during the reaction to improve the strength properties is more than that of glucose alone, especially at relatively high percentage of CMC.

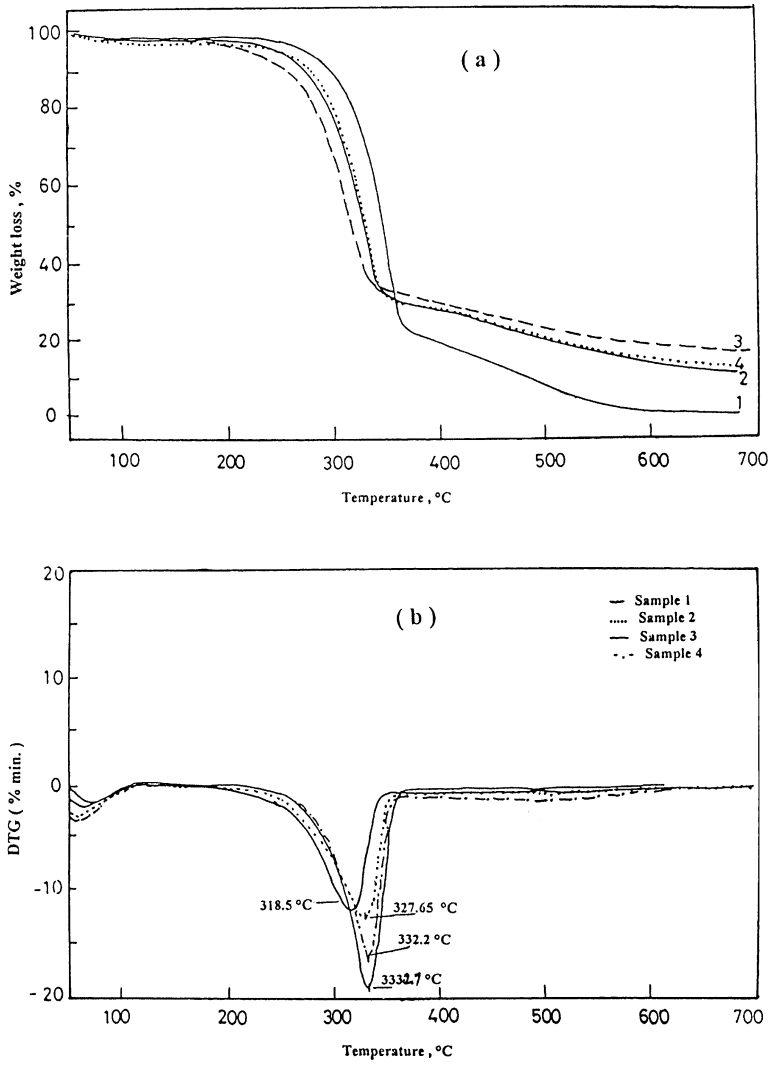

FIGURE 15 TGA and DTG thermogrames of untreated and treated paper samples.

– Increasing the percentage of cuprite in paper samples (Ash, % > 2.52%) has a deleterious effect on the strength properties of the sheets obtained; it also increases the electrical measurements.

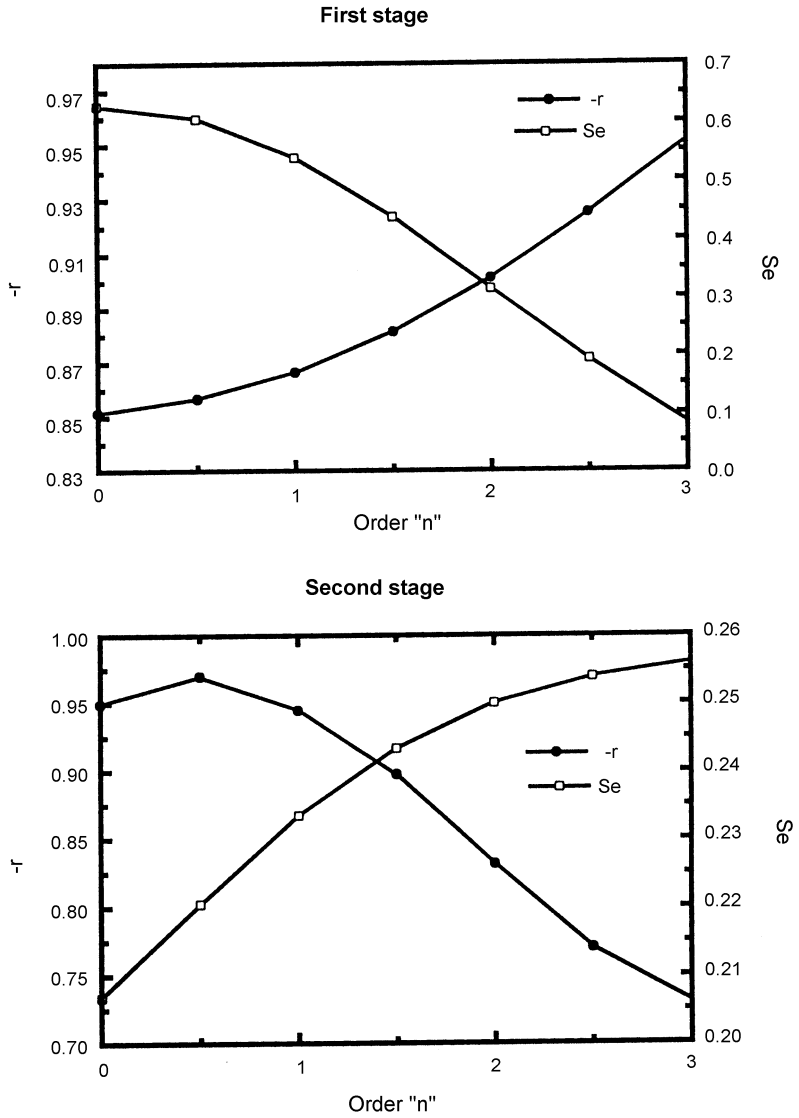

FIGURE 16 Statistical determination of "*n*" and Se of the main degradation stages of paper sheets prepared from untreated wood pulp.

– Addition of 60% glucose to 10% $CuSO_4$ during cuprite formation is the best condition for enhancing the paper fire retardency behaviour.

TABLE 4 Temperature ranges, order and Arrhenius parameters of the degradation stages of untreated and treated paper sheets

Sample no.	*Stage*	*Temp. range* °C	"*n*"	$-r$	*Se*	E_a *kJ/mol.*	A sec^{-1}	$k \times 10^4$ min^{-1}	*Weigh loss,*
1	1st stage	234.7–349.3	0.0	0.965	0.101	89.446	3.35×10^8	0.1994	77.2
	2nd stage	361.2–600	3.0	0.980	0.206	80.817	1.91×10^6	0.4801	16.5
2	1st stage	235.3–341.94	0.5	0.998	0.029	103.71	1.34×10^{10}	0.2849	68.1
	2nd stage	371.0–671.0	2.0	0.996	0.060	101.867	5.35×10^7	0.2827	18.8
3	1st stage	203.2–338.7	0.5	0.962	0.118	70.183	1.2×10^7	0.2334	64.5
	2nd stage	348.4–700.0	2.0	0.985	0.116	72.302	6.47×10^5	0.5280	16.2
4	1st stage	232.3–345.2	0.0	0.999	0.021	90.324	5.03×10^8	0.2226	68.0
	2nd stage	367.7–641.9	1.5	0.985	0.100	172.774	1.223×10^{14}	0.6801	15.3

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