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New approach for utilization of cellulose derivatives metal complexes in preparation of durable and permanent colored papers

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ABSTRACT

This work focused on studying the used of polymer complexes as a new approach for the preparation of high performance colored paper. In this respect, the paper strength, thermal stability, biological resistance, magnetic properties, as well as the durability of aged paper were evaluated. It was found that, using carboxymethyl cellulose–copper complexes [CMC–Cu(II)], as paper additive, enhances the strength properties of wood pulp paper sheet, and depends on the anion of the copper salt used and the pH-value during the preparation process. The best polymer complex is that produced from using copper sulfate as the origin of copper ion, at pH 5.4. Also, incorporating the CMC–Cu(II) complexes with wood pulp provides thermal stability, fire retardancy, biological resistance, magnetism, as well as durability to the paper sheets obtained.

1. Introduction

Colored paper has wide applications such as photographic paper, laminate and decorative base paper, cable paper, packing paper, wood-free-writing and printing paper, as well as magnetic and security paper. There are a number of requirements for colored paper considered in certain applications, especially as cable and laminate base paper for the furniture industry, and fine paper. Strength quality, longevity and heat resistance are the major requirements for such types of paper. There are two parts to a coloring system (Koretsky, 1983). The selection of the actual coloring agents, and (Ullmann's Encyclopedia of IndustrialChemistry, 1991). The method by which the colorants are attached to the substrate. Currently, the manufacture of colored paper is achieved by dyeing the paper stock, surface coloring in the size press, or surface coloring by coating, using dyes or pigments as coloring agents. Dyes are more affected by IR, UV & visible light due to photochemical reactions, causing fading of the color. The coloring agents that provide the best longevity are all pigments (not dyes). Unfortunately, pigments are insoluble and have no affinity to the substrate and require the use of binders. A common and economic way of retaining additives in paper pulp is by means of alum and rosin. This often results in an acidic paper and causes its deterioration on aging (El-Saied, Basta, & Abdou, 1998; Koretsky, 1983; VCH veriagsgesellschaft mbH, 1991).

Previously, our investigations were concerned with using new 3-pyridine-carbonitrile containing compounds and cellulose derivatives-metal complexes in preparation of security and high quality paper sheets [strength, thermal stability and magnetism (Basta, 1998; Basta & El-Saied, 2001; Basta, Zhan, & Chen, 2004; Basta, Girgis, & El-Saied, 2002; El-Saied, Basta, & Abde-El-Nowr, 1997)]. When the flame retardancy and biological resistance are required, it is necessary to provide such properties together with longevity to the colored paper.

Our previous experience covers manufacturing of permanence paper (Basta, 2003; Basta, 2004; El-Saied et al., 2000), and the preparation of organo-metallic compounds based on cellulose derivatives, in paper product and as novel adhesive for lignocellulosic composites (Basta, 1998; Basta & El-Saied, 2001; Basta, El-Saied, & Gobran, 2004; Basta, Zhan et al., 2004; El-Saied et al., 1997). In this work, we utilized CMC–Cu(II) complexes as a simple method of coloring paper pulp and for producing high performance wood pulp paper sheets, especially towards longevity (biological and thermal), fire resistance as well as magnetism.

2. Experimental

2.1. Materials and handsheets paper making

– Paper-grade wood pulp, as a paper substrate, was delivered from RAKTA Paper Mill, Alex., Egypt. The pulp was chemically analyzed as α-cellulose (Markblatt IV/29 Zellcheming), pentosan, (Jayme & Sarten, 1940), lignin (The Institute of Paper Chemistry, 1951) and ash.

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– Complexes of carboxymethyl cellulose with analytical grades of copper chloride, copper sulfate, and copper acetate were prepared and used as beater additives. The carboxymethyl cellulose was supplied from Hercules Inc. The average degree of substitution was determined by the conventional method (Basta, 1998). The preparation of the copper complexes was described in our previous work (El-Saied, Basta, Hanna, & El-Sayed, 1999).
– Handsheets of paper samples were prepared as the methods described elsewhere (El-Saied et al., 1997). The wood pulp together with copper complexes was beaten in a valley beater up to the degree of Shopper Reigler 50°SR (it's a measure of the drainability of a suspension of pulp in water). The beaten pulp produced (never dried) was adjusted to the desired pH by diluting acid or sodium hydroxide, then subjected to handsheet formation according to Swedish Standard method (S.C.A). 10% copper complexes were used in this investigation.

2.2. Measurements

– Strength properties: Copper complex-free or copper complex-containing paper samples were conditioned at a relative humidity 50% and temperature of 23 °C (ISO 187, 1990), and then tested for breaking length, burst and tear factors (The Institute of Paper Chemistry, 1952). For the purpose of comparison, the strength properties all together were expressed in the modified formula which has referred in reference (Basta, 1998), and known as the quality number (Q_z). The Q_z was calculated from summating the values of strength properties divided by number of properties minus one.
– Air permeability: This property can be obtained by measuring the resistance of paper sample of a given dimension to the passage of air under standardized conditions of pressure, temperature, and relative humidity. The values are expressed in arbitrary units as the amount of air passed in a given period of time (ml/min).
– Oil absorption was tested by using dyed caster oil. For measurement, a sizing "FRANK" tester was used.
– Roughness: The results are evaluated in term of the length of time taken for a given volume of air to pass between the sample and the articulating surface of the instrument.
– Wax number: The wax number or pick strength was tested to study the surface strength of handsheet produced. Dennison wax test was used in this study (Casey, 1981).
– Color strength: This property was tested by using Perkin Elmer Lamba 3B UV–vis Spectrophotometer.
– IR-spectra: IR-spectra (4000–200 cm^{-1}) were recorded on an Insco FT/IR-Infra red spectrophotometer using KBr disc method. The asymmetry index of the band corresponds to stretching vibration of hydroxyl groups, relative absorbance of hydroxyl and carbonyl groups, mean strength of hydrogen bond (MSHB), and crystallinity index were calculated as mentioned elsewhere (Basta, 1998; El-Saied et al., 1997).
– Magnetic measurements: Measurements of magnetic susceptibility (mass, c.g.s unit) were carried out using Gouy balance and $Hg[Co(SCN)_4]$ as calibrant. The behavior of the investigated copper complex-containing paper as magnetic paper were evaluated by comparing the obtained mass susceptibility values with that obtained from magnetic oxide (Fe_2O_3)-containing paper sheet.
– Biological evaluation: The anti-microbial actions of the paper samples on some bacteria (*Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Escherichia coli* NRRL B-210 and *Bacillus sabtilis* NRRL B-543), fungus (*Aspergillus niger*), and yeast (*Saccharomyces cerevisiae*), were carried out using the agar plate method (Abou-Zeid & Shehata, 1969).
– Accelerated aging: Paper samples were subjected to accelerating aging at 100 °C for 1, 3, 6, 9 and 12 days. 72 h at 100 °C is considered to be equal 25 years under ambient conditions (Kirova, Stepanova, Flyate, & Shul'man, 1997). Durability was estimated according to the equation described elsewhere (Basta, 2003; Basta, 2004).
– Thermogravimetric analyses (TGA and DTGA) were done using Perkin Elmer (Thermogravimetric Analyzer TGA7). Analysis was performed with a heating rate of 10 °C/min and nitrogen flow rate of 50 cc/min, under non-isothermal conditions.

2.2.1. TG-curve analysis

Kinetic studies based on the weight loss data were obtained by TG curve analysis. The activation energy was evaluated by applying Coat and Redfern method of analysis (Coat & Redfern, 1964). For pseudo homogeneous kinetics, the irreversible rate of conversion of the weight fraction of reactant may be expressed by the following equation:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (1)$$

where α is the fraction of material decomposed at time t, k is the specific rate constant and n is the order of reaction. The temperature dependence of k is generally expressed by the Arrhenius equation:

$$k = Ae^{-Ea/RT} \quad (2)$$

where A is the frequency factor (s^{-1}) and T is the absolute temperature.

For linear heating rate, a, (deg·min^{-1}):

$$a = \frac{dT}{dt} \quad (3)$$

For calculating the activation energy, E_a, of thermal decomposition when $n = 1$, Eq. (4) was used.

$$\log\left[\log\frac{1-\alpha}{T^2}\right] = \log\frac{AR}{aE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \quad (4)$$

Table 1
Chemical analysis of wood pulp and properties of its paper sheets

Property[a]	Value	SD[b]
α-Cellulose (%)	89.5	0.172
Pentosan (%)	8.7	0.00
Lignin (%)	Trace	–
Ash (%)	0.212	0.0113
Breaking length (m)	3540.12	6.5854
Burst factor [gf/(g/m^2)]	33.40	1.705
Tear factor[a] [(gf/cm^2)/(g/m^2)]	138.39	–
Permeability (ml/min)	350	7.439

[a] The test was carried on 4 strips.
[b] SD: standard deviation of 4 readings.

Table 2
Microanalytical data of CMC and its complexes

Proposed structure	C (%)	H (%)	Cu (%)[a]	H_2O molecule
CMC	40.3 (0.14)	4.9 (0.10)	–	–
$Cu(CMC)_2$[b]	38.3 (0.28)	3.5 (0.14)	53.7	–
Cu(CMC)·$2H_2O$[c]	34.0 (0.0)	5.1 (0.22)	71.0	2.3
Cu(CMC)·AcO[d]	43.2 (0.21)	4.9 (0.11)	58.6	–

The values between parentheses are standard deviation of 2 readings.
[a] Percentage of Cu(II) chelates with respect to the original amount.
[b] $CuCl_2$ is used as the origin of Cu(II) ion.
[c] $CuSO_4$ is used as the origin of Cu(II) ion.
[d] $Cu(AcO)_2$ is used as the origin of Cu(II) ion.

When $n \neq 1$, Eq. (5) was used;

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{aE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \qquad (5)$$

Plotting the left-hand-side value of the equation i.e., log $[1-(1-\alpha)^{1-n}/T^2(1-n)]$ against $1/T$ using various values of n should give a straight line with the most appropriate value of n (Basta, 1998). Least square method was applied for the equation, using values of n ranging from 0.0 to 3.0 in increments of 0.5 and calculating for each value of n, the correlation coefficient (r) and standard error (SE). The n value, which corresponds to the maximum r and minimum SE, is the order of the degradation process. The activation energies and frequency factors were calculated from the slope and intercept, respectively, of the Coat–Redfern equation with the most appropriate value of n.

3. Results and discussion

Table 1 represents the chemical constituents of the paper grade wood pulp used as a paper substrate and the properties of handsheet made from it. Table 2 shows the microanalysis of carboxymethyl cellulose (CMC) and its complexes with copper ions originated from different salts.

3.1. Strength properties of wood pulp paper sheets-containing CMC–Cu(II) complexes

Fig. 1 shows the effect of pH on individual properties of paper sheets, namely; breaking length, tear factor and burst factor, from pH 3.5 to pH 9.5, when CMC–Cu(II) complexes are added. The Cu(II) salts used were copper sulfate, copper chloride and copper acetate. Generally all properties increased as the pH is increased from 3.5 to about 5.0 and then decreased at higher pH-values. Using CMC–$CuSO_4$ as the additive gave the best improvement in strength quality at pH 5.4.

Fig. 1 also shows that the % ash increases as the pH is increased from 3.5 to 9.5 for all CMC–Cu(II) additives.

Fig. 2 summarizes the effect of pH on quality number (Q_z) for the same CMC–Cu(II) additives, where (Q_z) is the modified formula of all strength properties (Basta, 1998).

The observed improvement may be ascribed to the attraction of neutral or positively charged polymer complexes sphere to the negative charges known to exist on the fibers, i.e., cellulose fibers bridged through CMC–Cu(II) complex. Also, the presence of unchelated carboxy-methyl cellulose in the produced sheets causes an increase in Vander Waal's bonding, which supports the strength properties. While, the change in the strength properties and consequently the quality number as a function of pH-value and the ori-

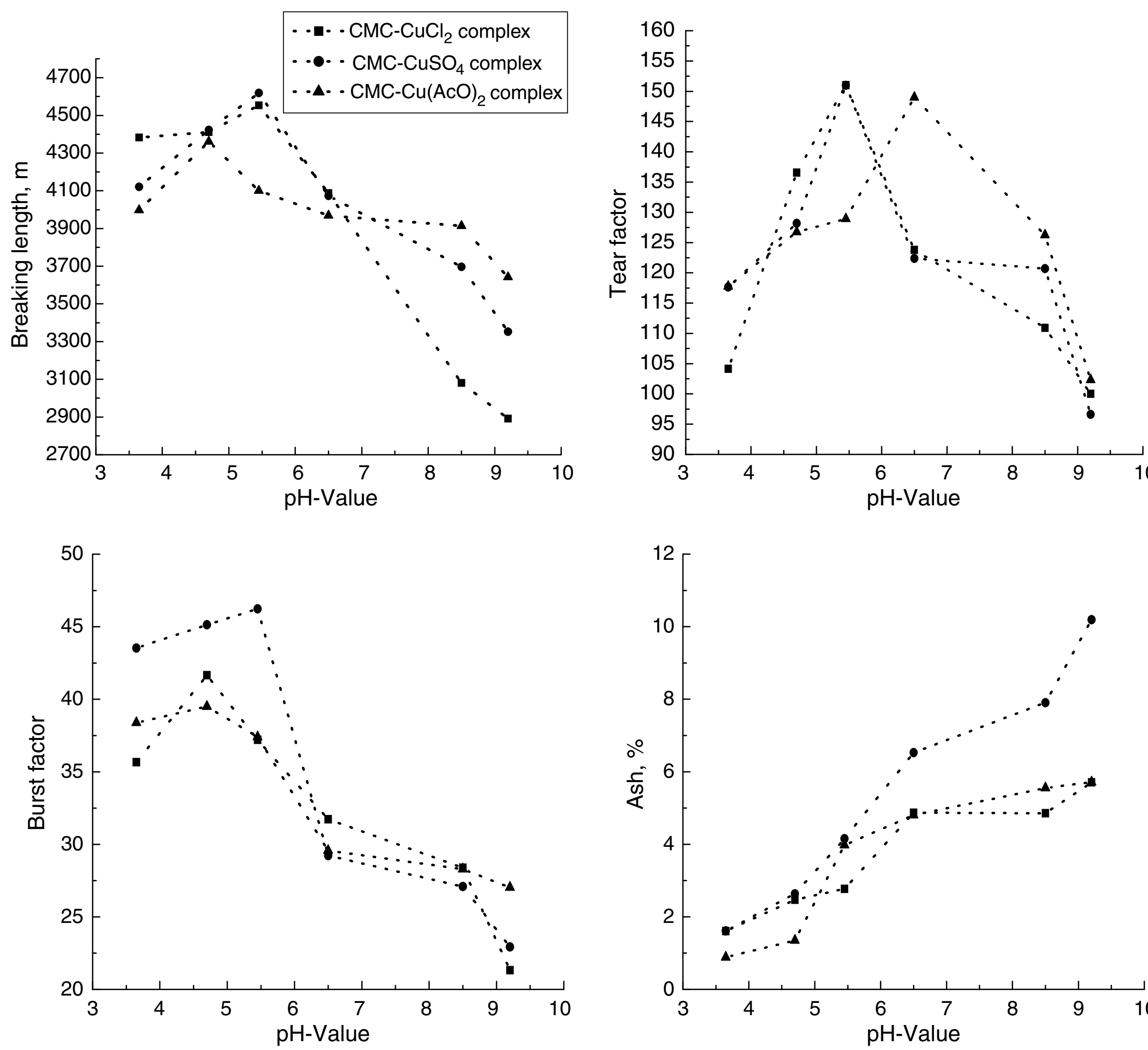

Fig. 1. Strength properties of CMC–Cu(II) complexes-containing wood pulp paper sheets.

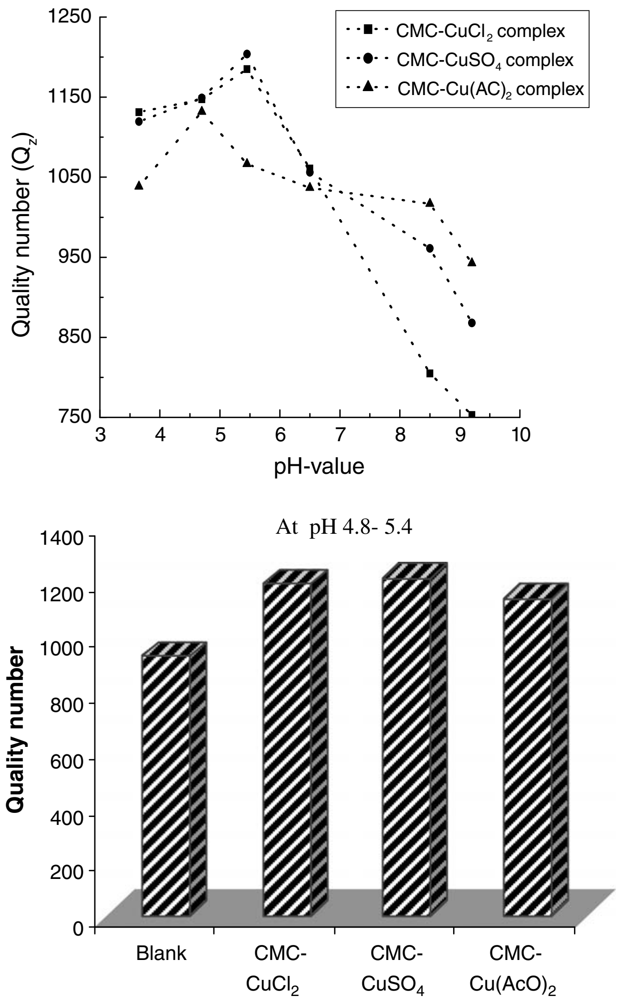

Fig. 2. Effect of pH on quality number (Q_z) of CMC–Cu(II) complexes-containing wood pulp paper sheets.

Table 3
IR-measurements of copper complexes-containing paper sheets

Complex	E_{OH}	$E_{C=O}$	Asymm. Index	MHBS	Cr.I.
–	1.48	0.81	1.7	1.5	1.2
$Cu(CMC)_2$	1.37	0.49	2.0	2.3	2.5
$Cu(CMC)·2H_2O$	1.24	0.44	2.1	2.0	2.6
Cu(CMC)·AcO	1.43	0.35	2.0	1.9	2.2

where, Asymm. Index of the bands correspond to stretching vibration of OH groups, MHBS is the mean hydrogen bond strength, and Cr.I. is the crystallinity index (A_{1430}/A_{900}).

gin of Cu(II) ion this probably the result of the pH dependence in the adsorption or desorption of copper (II) ions, in $Cu(Ac)_2$ via the carboxymethyl groups and exhibits the formula $[Cu(CMC)_2]$ and [Cu(CMC)AcO], respectively; while it acts as a binegatively charged bidentade ligand when it is chelated with $CuSO_4$ via the carboxymethyl and secondary hydroxyl groups and exhibit the formula $[Cu(CMC)·2H_2O]$ (El-Saied et al., 1999). These formed bonds are low stable in acidic medium (Pasteka, 1992). This view is emphasized from the decrease of ash content of acidic medium prepared sheets, especially on using $CuCl_2$ as the origin of Cu(II) ion, compared to those prepared in neutral and alkaline media (Fig. 1). However, due to oxidation effect of formed $CuCl_2$, at acidic pH-value using dilute HCl, to some hydroxyl groups, destruction of weak hydrogen bonds and subsequent reordering of the chains with the formation of new and relatively stronger hydrogen bonds (Table 3). This leads to improved strength properties of produced sheets in case of using $[Cu(CMC)_2]$ compared to those prepared from $[Cu(CMC)·2H_2O]$ and [Cu(CMC)·AcO].

As can be seen, elevating the pH-value during paper sheet preparation by dilute NaOH to alkaline range, pH 8–10, is accompanied by a reduction in the level of strength improvement or deterioration in strength properties of polymer complex-wood pulp sheets. The explanation of these data is probably ascribed to the competition of Na ions with Cu(II) ions or complex sphere to attract on the negative charge of cellulose fibers surface. The presence of univalent sodium ions have no power to form a bridge between the cellulose fibers, as the case of CMC–Cu(II) complexes, and in the same time diminishes the formation of hydrogen bond between the hydroxyl and carbonyl groups. In other words, the presence of sodium ions reduces the probability of bridging of the cellulose fibers through complex sphere. To confirm this view further measurements are carried out, such as roughness, permeability, oil penetration or absorption as well as wax pick. These measurements are recorded in Table 4. It's obvious that, elevating the pH-values by sodium hydroxide during sheet formation leads to weakness the bond possible formed (intra and inter) between CMC–Cu(II) complexes and hydroxyl group on wood pulp constituents. This accompanied by increasing the voids between fiber chains, roughness, and fasting migration of the oil inside paper, compared to that made in neutral pH-value.

3.2. Thermal properties of CMC–Cu(II) complexes-wood pulp paper sheets

The thermal analysis of the wood pulp paper sheets-containing copper complexes was carried out as a preliminary study of the effect of accelerated aging on the properties of the paper sheets, as well as the fire retardancy behavior. TGA and DTG curves of investigated paper sheets are shown in Fig. 3.

From Fig. 3, it is seen that three degradation stages are observed in case of the wood pulp paper sheets without CMC–Cu(II) complexes. The first stage at a temperature peak of ~62 °C is due to the loss of the absorbed moisture. At temperature region 234.7–350 °C, the degradation stage are due to the decomposition of wood pulp constituents (depolymerization, thermooxidation, and dehydration (inter- and intra-molecular). This stage control the yield of levoglucosan, which is considered the source of the fuel for the flame (volatilization) (Shafizadeh, Lai, & McIntyer, 1979), and known as the main degradation stage. At higher temperature

Table 4
Physical measurements of $Cu(CMC)·2H_2O$ complex-containing paper sheets

pH-value	Permeability ml/min	Roughness		Oil penetration sec.		Wax No.
		Side a	Side b[A]	Side a	Side b	
3.65	300 (8.66)	590 (5.0)	680 (4.6)	9 (0.849)	18 (0.44)	14
~6.0	190 (12.8)	560 (13.2)	695 (6.35)	22 (1.04)	28 (0.48)	14
9.2	260 (5.47)	615 (9.64)	760 (6.5)	4 (0.49)	5 (0.39)	10

The values between parentheses are standard deviation of 4 readings.
[A] Side was contacted to wire of paper machine.

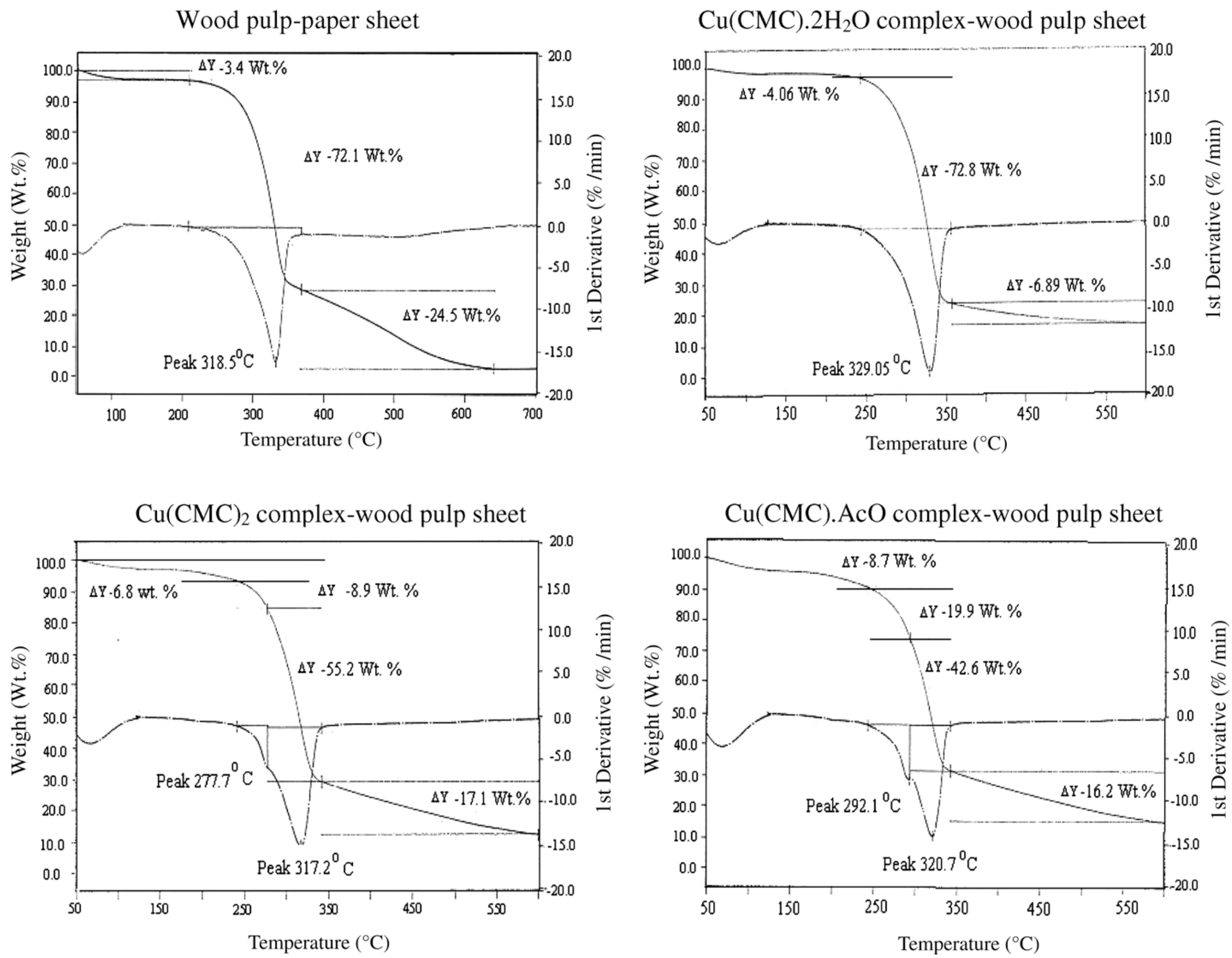

Fig. 3. TGA and DTG of wood pulp and copper complexes-containing wood pulp paper sheets.

Table 5
Thermal degradation measurements of copper complexes-containing paper sheets in comparison to wood pulp sheet (Main degradation stage)

Complex	Temp. range (°C)	DTG Peak (°C)	Order "*n*"	$-r$	SE	E_a (kJ/mol)	Weight remain (%)
–	234.7–349.3	318.5	0.0	0.965	0.101	89	24.52
$Cu(CMC)_2$	241–276	277.7	1.0	0.997	0.0396	273.34	29.17
	277.7–341.8	317.2	1.0	0.99	0.0615	<u>203.15</u>	
						Σ 476.49	
$Cu(CMC)\cdot 2H_2O$	241.9–293.1	292.1	0.5	0.995	0.0464	161.85	31.904
	293.1–341.9	320.7	1.5	0.996	0.0561	<u>352.39</u>	
						Σ 514.24	
$Cu(CMC)\cdot AcO$	244.2–356.7	329.1	0.5	0.995	0.0113	102.66	23.46

Where, *r* is correlation coefficient, SE is standard error estimate, and E_a is the activation energy of the main degradation stage.

Table 6
Anti-microbial action of copper complexes-containing paper sheets on some microorganisns

Complex	*Pseudomonas aeruginosa*	*Staphylococcus aureus*	*Escherichia coli*	*Bacillus sabtilis*	*Aspergillus niger*	*Saccharomyces cerevisiae*
–	−ve	−ve	−ve	−ve	−ve	−ve
$Cu(CMC)_2$	−ve	++	+	+	−ve	++
$Cu(CMC)\cdot 2H_2O$	−ve	+++	+	+	+	++
$Cu(CMC)\cdot AcO$	−ve	++	++	++	+	++

−ve value: there is no inhibition effect to tested microorganism.

Table 7
Magnetic behavior of copper complexes and magnetic filler-containing paper sheets

Complex	Mass susceptibility (X_g; c.g.s.)
–	–
Cu(CMC)$_2$	3.99×10^{-7}
Cu(CMC)·2H$_2$O	4.65×10^{-5}
Cu(CMC)·AcO	1.27×10^{-6}
Fe$_2$O$_3$	5.59×10^{-6}

(361–600 ° C), the degradation stage is due to rapid volatilization accompanied by the formation of carbonaceous matter. The DTG curves show the rate of weight loss related to the main decomposition of wood pulp sheet at 318.5 °C.

The behavior of copper complexes-containing paper sheets on the thermogram shape shows difference compared to wood pulp sheet alone. Incorporating [Cu(CMC)$_2$] and [Cu(CMC)·2H$_2$O] complexes (Fig. 3) show additional peaks at relatively low DTGA peak temperatures for the stages responsible for the formation of levoglucosan (main stage). In the same time these stages are started at a relatively high temperature and the weight loss of volatilization stage neared completion at relatively low temperature resulted the relatively high weight remain percentage, compared to wood pulp sheet, i.e., reduction of formation of levoglucosan is occurred [Table 5].

It is interesting to note that, the three investigated copper complexes not only lead to increasing the thermal stability of the paper, but these complexes, especially based on CuCl$_2$ and CuSO$_4$, also retard the rate of mass loss with remaining values of about 29–31.9%. In other words, these complexes provide additional fire resistance property through minimizing the formation of levoglucosan, and consequently reduce the formation of toxic gases.

The activation energies shown in Table 5 demonstrate that the E_a's of the degradation stage, corresponding to the creation of levoglucosan in complexes-containing paper sheets are higher than E_a of wood pulp. These data demonstrate that the presence of copper complexes enhances the dehydration stage than depolymerization and formation of levoglucosan, and thus result in high thermal stability. This observation is ascribed to additional bond formation (coordinated bond) between copper complexes and wood pulp fibers, as well as hydrogen bonds. Polymer complex based on CuSO$_4$ achieves the best fire resistance behavior. The thermal measurements are in agreement with the data of FTIR-spectra [crystallinity index (CI) and mean hydrogen bond strength (MHBS)].

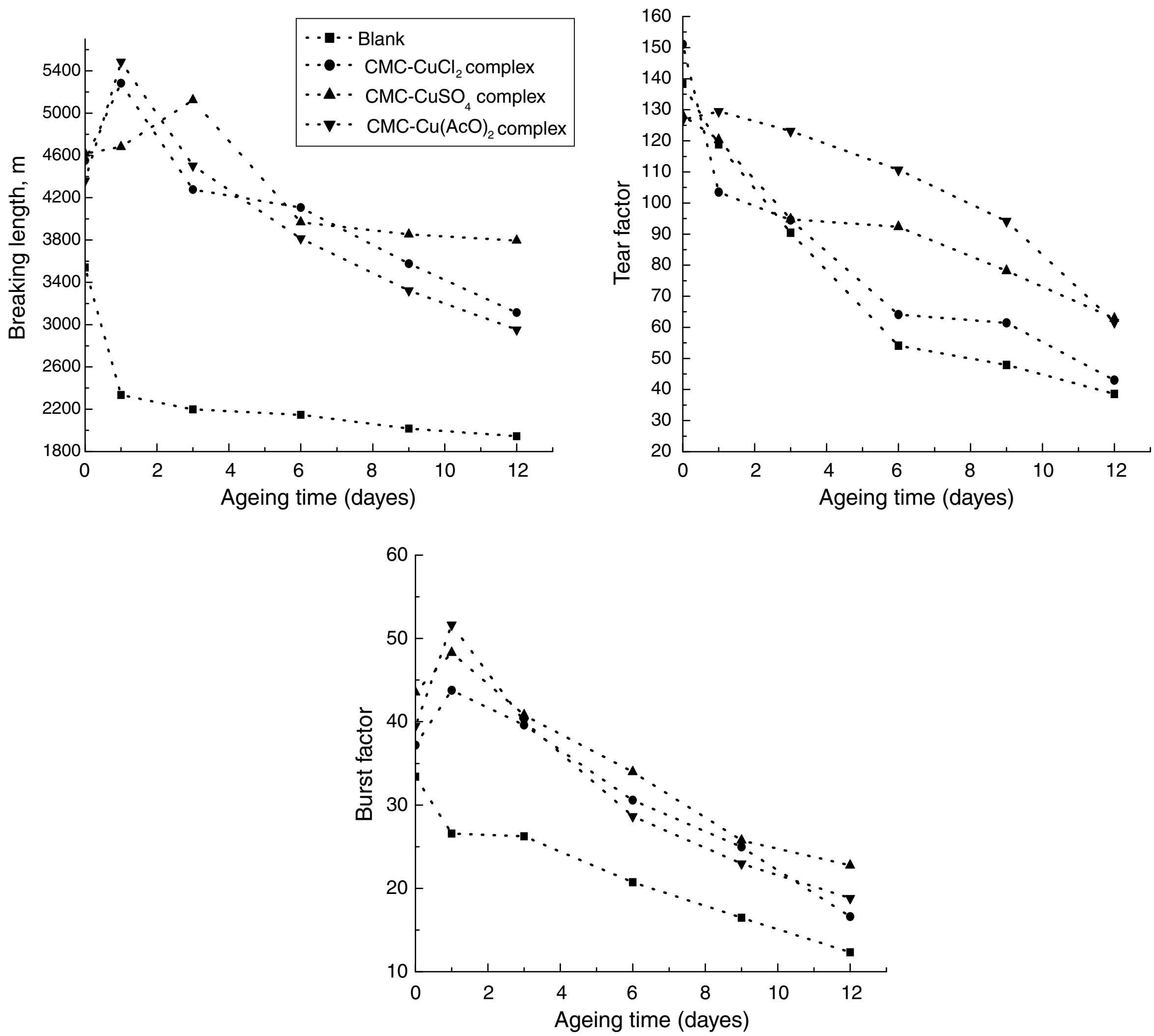

Fig. 4. Effect of incorporating copper complexes to wood pulp on strength properties of obtained sheets toward accelerated aging.

3.3. Biological resistance of CMC–Cu(II) complexes-wood pulp paper sheets

The data obtained in Table 6 show that, incorporating CMC–Cu(II) complexes to wood pulp have inhibiting effect to all tested microorganisms except bacteria of the type *Pseudomonas aeruginosa*. Also, Cu(II)-complex originated from using $CuCl_2$ no inhibiting effect on fungus (*Aspergillus niger).* The highly inhibiting effect is noticed on using Cu(II)-complex-based on $CuSO_4$. This highly inhibiting effect is probably ascribed to its higher metal percentage, compared to other salts, which is reflected in the ash content of the paper sheets produced.

3.4. Magnetic property of CMC–Cu(II) complexes-wood pulp paper sheets

To evaluate the role of copper source in complex formation and consequently the bond formation between CMC and Cu(II) ions, as well as Cu complex with functional groups of wood pulp constituents, the magnetic properties of the copper complexes-wood pulp paper sheets are compared. Table 7 shows that, incorporating copper complex, using copper sulfate as the origin of Cu(II) ions, provides relatively high magnetic properties. The mass susceptibility (X_g; c.g.s) of the paper sheets obtained decreases in the order $CuSO_4 > Cu(AcO)_2 > CuCl_2$.

The relatively low mass susceptibility in case of $CuCl_2$ is ascribed to the formation of CMC–Cu(II) complex $[Cu(CMC)_2]$, where the lone pair of electrons of aliphatic ether and the carboxyl groups of carboxymethyl cellulose are coordinated together with Cu(II) ions of $CuCl_2$ salt. However, the liberation of hydrogen atoms from the secondary hydroxyl group of CMC to coordinate with Cu(II) is more possible than the coordination of the lone pair electron on oxygen of ether linkage in complexes from copper salts of sulfate and acetate anions. It is interesting to note that the mass susceptibility of the investigated paper when using $CuSO_4$ is higher than that produced from adding known magnetic pigment, such as Fe_2O_3.

3.5. Evaluation of CMC–Cu(II) complexes in the production of durable paper sheets

From the foregoing results it can be concluded that, incorporating the CMC–Cu(II) complex in paper sheet gives positive effect on strength, thermal stability, and magnetic behavior, as well as provides it fire and biological resistance. These encouraging data led us to study the longevity of these high quality colored papers. Previous studies revealed that the main parameters of the deterioration of paper documents are the chemical composition of the paper and ink (Havlimova et al., 2002). Other contributing factors are the storage conditions, such as heat and humidity. In this work we applied the dry heat treatment at 100 °C in the investigation of accelerated aging for wood pulp and copper complexes-wood pulp paper sheets (at optimum pHs). It is considered that three days under these conditions correspond to 25 years of natural aging (Kirova et al., 1997). The changing of strength and color strength of all investigated paper sheet against the time of accelerated aging are illustrated in Figs. 4 and 5.

It can be seen from Figs. 4 and 5 that generally, a significant decrease in paper strength and change in color strength are noticed upon accelerated aging. The relatively high change is observed in the case of free complex-paper sheet compared to copper complexes-containing-paper sheets. The deterioration rate in the former paper is caused by one day of aging, while incorporating the complexes allows the deterioration rate to start after 3–6 days. The loss of the strength of wood pulp paper upon accelerated aging is related to a decrease in the fiber strength as a result of cellulose depolymerization and to oxidation of lignin and hemicellulose which leads to the formation of additional carboxylic groups.

There is an exponential relation between the reduction of carbonyl groups (chromophores formed) and discoloration (Basta, 2003; Basta, 2004; Havlimova et al., 2002). In our investigated paper samples, the polymer complexes scavenge the hydroxyl groups of wood pulp constituents through bond formation, and consequently protect it to some extent from oxidation.

As can be seen, at aging time from 1 to 6 days, [Cu(CMC)·AcO] complex achieves high durability (Fig. 5), compared to other complexes, and the $[Cu(CMC)_2]$ complex has the lowest durability. However, the reverse trend is observed at higher aging time (9–12 days), where paper prepared from the acetate complex has the same durability as that produced from $[Cu(CMC)_2]$ complex, whereas the copper complex-based on copper sulfate achieves high durability. This may be ascribed to cleavage of the acetate group contained in the polymer complex upon accelerated aging, and consequently increases the acidity of the paper from its reaction with absorbed water in the sheet.

4. Conclusions

- All the investigated CMC–Cu(II) complexes, as paper additives, had positive effects for improving the quality of obtained paper sheets.

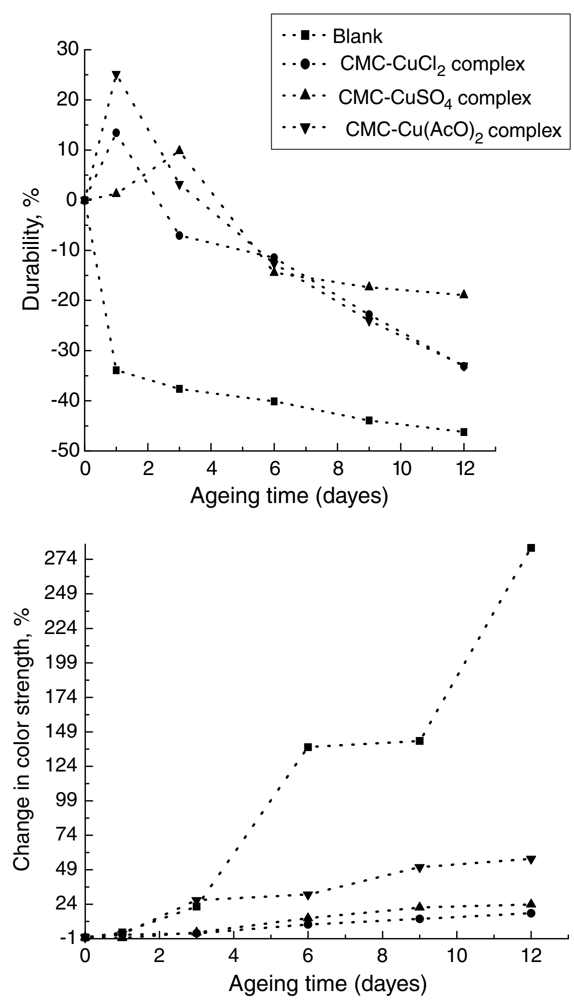

Fig. 5. Effect of incorporating copper complexes to wood pulp on durability and change in color strength of obtained sheets toward accelerated aging.

- Improvement in strength properties is dependent on the anion of copper salts and pH-value during the preparation process. Incorporating the CMC–Cu(II) complex, using $CuSO_4$ as the origin of Cu(II) ions, at pH 5.4 achieved the best improvement in strength quality.
- Incorporating CMC–Cu(II) complexes, using $CuCl_2$ and $CuSO_4$ as a source of Cu(II) ions provided fire retardancy, thermal stability and durability to the obtained paper. Whereas, complexes from $CuSO_4$ provided anti-microbial and magnetic properties with less change in color strength upon accelerated aging.

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