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Some Properties of Wood Pulp-Polymer Complexes Paper Sheets

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A new type of insulating wood pulp-polymer complexes paper sheets has been developed. The effect of variation of pH-value, during preparation process, on mechanical properties of the prepared sheets was studied. The prepared sheets were also subjected to electrical and IR-spectrophotometric studies. The results obtained show that the type of polymer ligand (HEC, PVA & CMC), cation (Fe^{3+} & Zn^{2+}) and anion (Cl^- & NO_3^-) of the metal salts of polymer complex, in addition to the pH-value have a profound effect on the mechanical properties of the prepared sheets. The optimum properties were obtained in case of beater addition CMC-Zn(II) complex at pH 6.62. The high insulation properties of the prepared sheets containing polymer complexes [CMC-ZnCl₂ & CMC-Fe(NO₃)₃] were noticed, compared with those obtained from addition of metal salts (FeCl₃) or wood pulp without additives.

The results of dielectric constant (ϵ') and dielectric loss (ϵ'') in some cases are in good agreement with the IR-measurements. However, the IR-measurements are in agreement with the strength properties.

Keywords: Wood pulp; polymer complexes; polymer ligands' mechanical properties; dielectric properties

INTRODUCTION

Paper is the cheapest and best electrical insulating materials known. The important electrical properties for good electrical insulation paper are [1]: 1-high dielectric constant (specific inductive capacity), 2-high dielectric strength (electrical resistance), 3-low power factor (dielectric loss), and 4-freedom from conducting particles.

Trials have been made by numerous investigators to improve the electrical properties of cellulose paper (reduce the dielectric loss and increase the dielectric constant), to meet the different applications, especially as insulating material for electrical equipment which needs a higher voltages (>500 kV). Such attempts include modification of paper substrate, e.g., oxidation [2], impregnation of cellulose paper with insulating oils [3–5], and replacing the cellulose fibres by some synthetic materials that exhibit better dielectric properties than cellulose, e.g., polypropylene fibre [6, 7].

The literature also revealed that, the electrical properties of cellulose materials increased when it is treated with ferric chloride [8].

In our previous work [9–13], the preparation and characterization of trivalent [Cr(III) & Fe(III)] and divalent [Co(II), Ni(II) and Cu(II)] metal ions with cellulose ethers (CMC & HEC) have been described. Fe(III)-cellulose ethers complexes have a relatively high stability than other metal ions [13]. Complexes of CMC with Cu(II) ions of CuCl_2 and CuSO_4 were suitable to use as a semiconductor materials [14].

Based on the foregoing literature, the present investigation is concerned to study the effect of polymer complexes addition on the mechanical and electrical (dielectric constant & dielectric loss) properties, in addition to IR-measurements of produced wood pulp paper sheets. The properties of paper sheets prepared from FeCl_3 addition to wood pulp are taken for comparison.

EXPERIMENTAL

Materials

a-Paper Substrate

Paper grade kraft soft wood pulp samples was delivered from Rakta Paper Mill, Alexandria, Egypt. The pulp was analysed as follows:

- (i) α -Cellulose estimation was carried out according to Markblatt IV/29 Zellcheming (German Association of Cellulose Chemist & Engineering).
- (ii) Pentosan was estimated according to Jayme and Sarten (15).

- (iii) Lignin estimation was carried out according to the Institute of Paper Chemistry [16].
- (iv) Ash content was determined by ignition in a muffle furnace at 400°C for one hour, then at 850°C for 45 minutes.

b-Additives

Polymer complexes from polyvinyl alcohol (PVA), hydroxyethyl cellulose (HEC), and carboxymethyl cellulose (CMC) with analytical reagent grades of FeCl_3 , $\text{Fe}(\text{NO}_3)_3$ and ZnCl_2 were used as a beater additives. The PVA (Mowiol type) used as a ligand was purchased from Hoechst Co.; while, the cellulose ethers (HEC & CMC) were purchased from Fuluka Chemical Co. The preparation of the polymer complexes as the method described in our previous work [13].

Handsheets Paper Making and Strength Properties Measurement

The prepared complex (30% based on pulp) was added to wood pulp before beating, the processes was continued to SR^o42–47 for paper sheet making.

Paper sheets were made, at different pH's, according to the Swedish standard method (S.C.A.). The prepared paper sheets were conditioned at relative humidity 65% and temperature 20°C. Then they were tested for breaking length, burst and tear factors [17]. The ash content of prepared sheets was also estimated, as an indication to the metal content in paper samples.

For each test at least five measurements were carried out, and the arithmetic mean of the obtained results was calculated.

Dielectric Measurements

The dielectric constant (ϵ') and dielectric loss (ϵ''), were measured using an NF Schering bridge type decameter DK 05 from WTW Germany in frequency range 500 Hz to 50 kHz. A guard-ring capacitor type NFM/5T was used. The accuracy of the measurements of ϵ' and ϵ'' were $\pm 1\%$ and $\pm 3\%$, respectively. Paper sheets subjected to this study were heated to constant weight in an electric oven and then kept

over phosphorous pentoxide before measurement. The measurements were carried out at room temperature: $\sim 25^{\circ}\text{C}$.

Conductivity Measurements

The d.c. conductivity of the samples were measured using a simple power supply unit GM 4561/01 from Philips to give a stable d.c. voltage between 0 and 150 volts with a maximum permissible loading current of 1mA. The potential difference (V) between the plates holding the sample and the current (I) flowing through it were measured using an ultimeter type ORI/BN 1050 from Rhode and Schwarz, Germany.

Infra-Red Absorption Spectra

Spectra of untreated and polymer complexes addition paper sheets were obtained in the region from $4000\text{--}200\text{ cm}^{-1}$, under identical conditions. The apparatus used was Inco FT/IR-300E, Fourier Transform Infrared Spectrometer, using the KBr disc technique.

RESULTS AND DISCUSSION

Table I represents the chemical constituents of the wood pulp under experimentation and the properties of handsheet made from it without additives; while Table II shows the micro-analysis of polymers used and their complexes with Fe(III) and Zn(II) ions.

The effect of using the polymer complexes as beater additives on the mechanical and electrical properties, in addition to IR-Spectra

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

<i>Property</i>	<i>Mean value</i>
α -Cellulose, %	86.550
Pentosans, %	7.000
Lignin, %	Trace
Ash, %	0.187
Breaking length, m	4539.353
Burst factor	33.069
Tear factor	108.071

TABLE II Micro-analysis of polymers and their complexes with metal ions

Sample	C, %	H, %	Metal, %	Cl, %	N, %	H ₂ O* molecule
PVA	55.04	8.90	—	—	—	—
PVA-FeCl ₃ complex	52.26	8.46	10.49	3.13	—	—
HEC	47.90	6.06	—	—	—	—
HEC-FeCl ₃ complex	29.50	3.80	15.10	18.90	—	—
CMC	39.60	5.29	—	—	—	—
CMC-FeCl ₃ complex	29.30	4.70	15.80	17.40	—	3.00
CMC-Fe(NO ₃) ₃ complex	24.65	3.90	15.26	—	6.10	3.00
CMC-ZnCl ₂ complex	33.26	5.08	13.83	3.64	—	0.70

*The no. of water molecules was calculated from the difference between H, % calculated and found, taken into account the moisture content in sample (13).

measurements of the prepared sheets are illustrated in Figures (1–6) and Tables (III–VI).

Mechanical Properties

The mechanical properties of paper sheets prepared from adding different types of polymer complexes to wood pulp (W.P.) were measured and illustrated graphically in Figures (1–3), as a function of pH during preparation process. The effect of FeCl₃ addition was used for comparison.

From Figure 1 it is clear that, addition of FeCl₃ and polymer-FeCl₃ complexes (except PVA-Fe(III) complex), to wood pulp have a positive effect on the strength properties (breaking length, burst factor and tear factor) of produced paper sheets. The improvement in strength properties in case of FeCl₃ addition is probably due to the attraction of multivalence ferric ions by the negative charges known to exist on the cellulose fibers, i.e., cellulose fibres bridged through Fe(III) ions; while, in case of polymer complex addition the cellulose fibres surface are probably bridged through the charged polymer-Fe(III).

Figure 1 also showed that, the change in strength properties was accompanied the type of cellulose ether used as a ligand in complex formation. CMC-complex addition exhibits high strength properties than HEC-complex. This is related to the nature of functional groups in cellulose ether (ligand), and consequently the bond strength of ferric ions with it. Whereas, the carboxyl anion have a high adsorption capacity than hydroxyl groups [18].

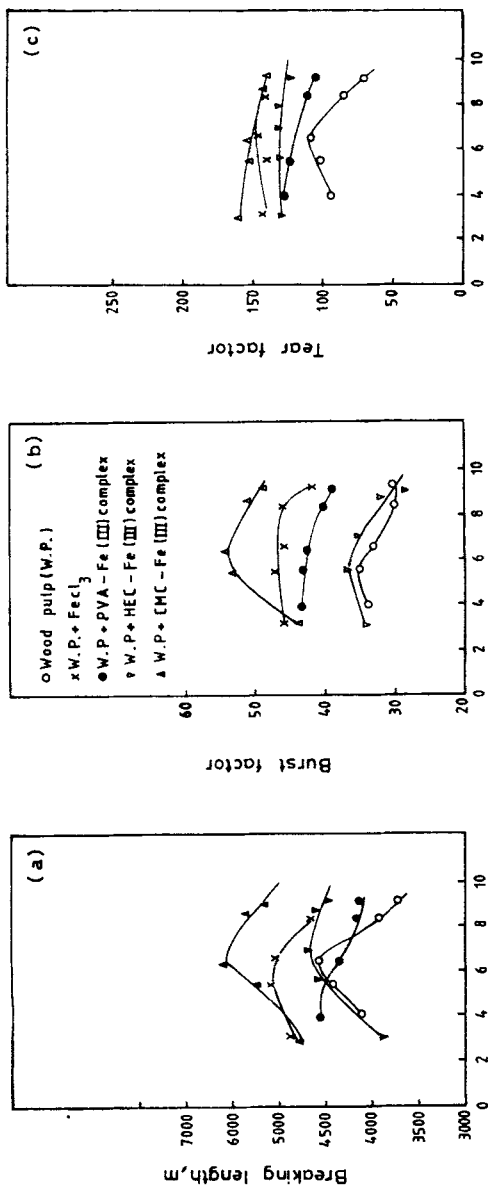


FIGURE 1 Effect of polymer complex and the type of ligand polymer on the mechanical properties of paper sheets, at different pH's.

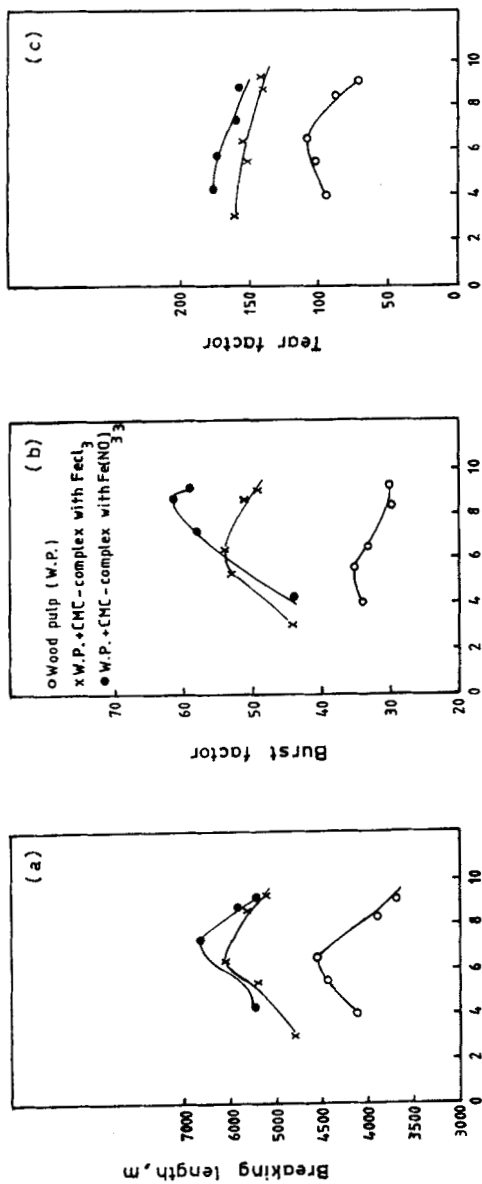


FIGURE 2 Effect of anion of metal salt used for complex formation on the mechanical properties of paper sheets, at different pH's.

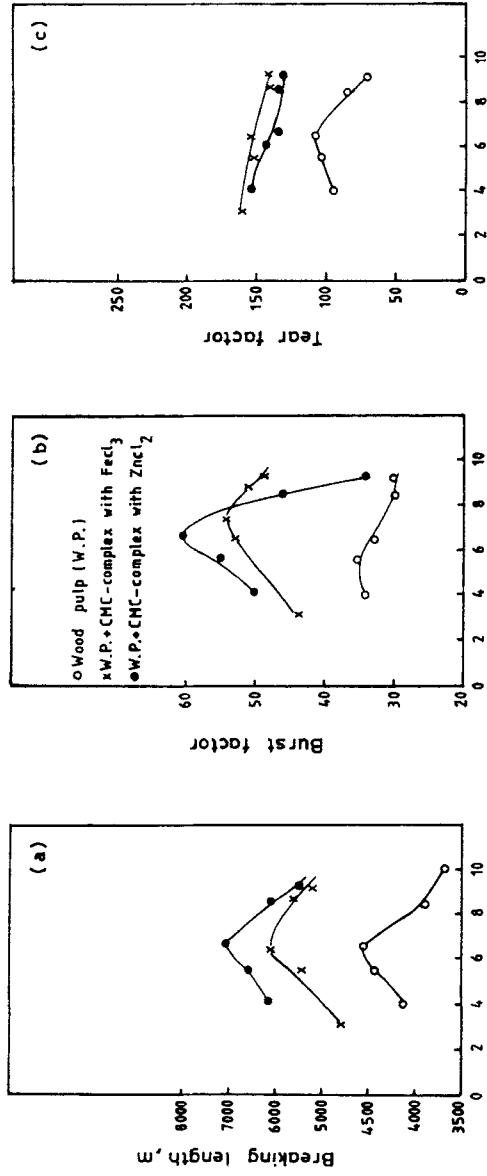


FIGURE 3 Effect of cation of metal salt used for complex formation on the mechanical properties of paper sheets at different pH's.

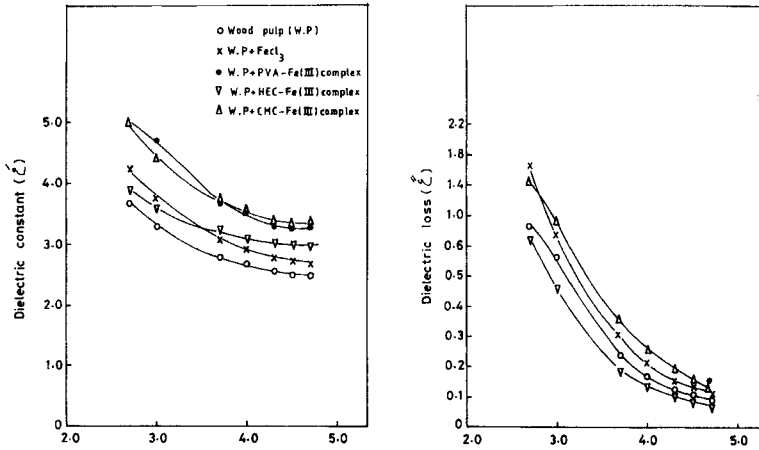


FIGURE 4 Variation of dielectric properties (ϵ' and ϵ'') with frequency of paper sheets obtained from various ligand polymer complexes addition.

The variation of pH-value of paper sheet preparation process either by dilute HCl or NaOH was also affected on the strength properties. This is probably the result of the pH dependence in the adsorption or desorption of Fe(III) ions, in addition to the stability of the bonds of ferric atoms with glucose of cellulose chains; whereas, these bonds are low stable in acidic medium [19]. This view is emphasized from the decrease of ash content of acidic medium prepared sheets compared with those prepared in neutral and alkaline pH's (Tab. IIIa).

Elevating the pH during paper sheet preparation by dilute sodium hydroxide to alkaline range reduces the improvement in strength properties of prepared sheets, compared with those produced at pH 6–7. This is probably due to the competition of Na ions with Fe (III) ions of FeCl₃ salt or complex sphere to attract on the negative charge of cellulose fibres surface. The presence of univalent sodium ions have no power to form a bridge between the cellulose fibres, as the case of multivalent ferric ions, and in the same time diminishes the hydrogen bond formed between the hydroxyl groups.

The deterioration of strength properties, at all pH-values, in case of PVA-FeCl₃ complex addition (Fig. 1) may be attributed to decrease the adsorption of Fe(III) ions of PVA during complex formation (less ash content; Tab. III-a), which contains no carboxyl or carbonyl

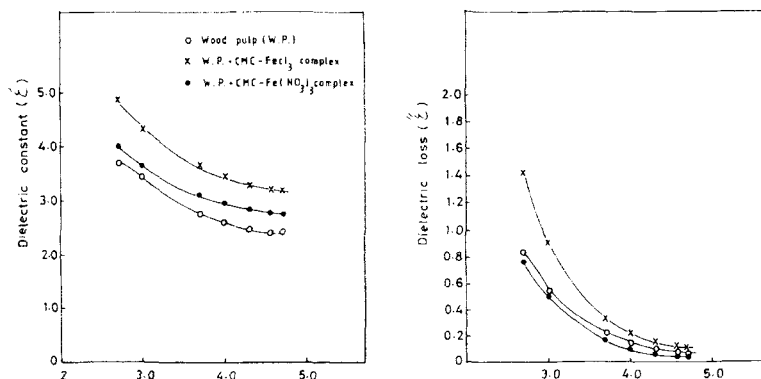


FIGURE 5 Variation of dielectric properties (ϵ' and ϵ'') with frequency of paper sheets obtained from changing the anion of metal salt of polymer complex addition.

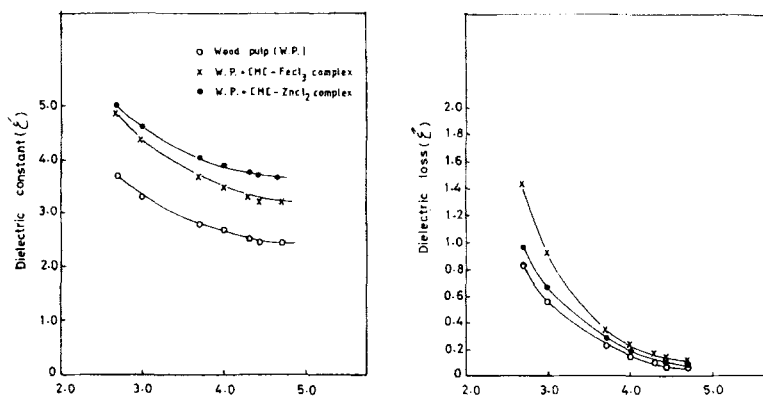


FIGURE 6 Variation of dielectric properties (ϵ' and ϵ'') with frequency of paper sheets obtained from changing the cation of metal salt of polymer complex addition.

groups as in case of cellulose ethers (HEC & CMC), consequently the bridging of the cellulose fibres through complex sphere also reduces.

Figure 2 shows the effect of anion of ferric salt used for complex formation with CMC on the strength properties of the prepared sheets. It is clear that using FeCl₃ or Fe(NO₃)₃ as a source of Fe(III) ions in CMC-complex formation improves the strength properties of prepared sheets. The extent of the improve in case of CMC-Fe(NO₃)₃ is higher than CMC-FeCl₃ complex addition, especially at neutral pH;

TABLE III Effect of FeCl_3 and polymer complexes addition on ash content of produced paper sheets, at different pH's

a-Effect of ligand polymer type									
Wood pulp		FeCl_3		PVA- FeCl_3 complex		HEC- FeCl_3 complex		CMC- FeCl_3 complex	
pH	Ash, %	pH	Ash, %	pH	Ash, %	pH	Ash, %	pH	Ash, %
3.99	0.365	3.23	5.030	3.85	3.622	3.10	5.589	3.06	5.5
5.48	0.193	5.48	6.606	5.48	3.462	5.59	7.527	5.45	7.653
6.53	0.210	6.65	7.424	6.36	3.918	7.08	8.915	6.36	10.400
8.40	0.389	8.44	8.024	8.36	5.971	8.84	8.649	8.68	10.979
9.12	0.829	9.20	9.511	9.15	5.629	9.12	9.860	9.19	11.712

b-Effect of anion and cation of metal salt							
Wood pulp		CMC- FeCl_3 complex		CMC- $\text{Fe}(\text{NO}_3)_3$ complex		CMC- ZnCl_2 complex	
pH	Ash, %	pH	Ash, %	pH	Ash, %	pH	Ash, %
3.99	0.365	3.06	5.000	4.18	6.752	4.05	1.137
5.48	0.193	5.45	7.650	5.68	7.096	5.98	2.504
6.53	0.210	6.36	10.400	7.32	7.690	6.62	5.271
8.40	0.389	8.68	10.979	8.75	7.110	8.50	9.491
9.12	0.829	9.19	11.712	9.16	9.737	9.19	8.515

6.5–7.4. This result may be related to the values of nephlauxetic parameter (β) of complexes under investigation; whereas, the values of (β) in case of CMC- FeCl_3 and CMC- $\text{Fe}(\text{NO}_3)_3$ complexes are 0.43 and 0.45, respectively [13]. According to Jørgensen [20] a decrease in the nephlauxetic parameter (β) is associated with a reduction in nuclear charge on the cation, consequently, the Fe(III) ions of CMC- FeCl_3 complex is less probable to bridge the cellulose fibre surface compared to CMC- $\text{Fe}(\text{NO}_3)_3$ complex.

Again, it is clear that (Fig. 2), using $\text{Fe}(\text{NO}_3)_3$ salt, during complex formation, diminishes the decrease in the improvement of strength properties as a result of acidic ($\text{pH} < 5.0$) preparation paper sheets of CMC- FeCl_3 complex addition. This is related to the stability constant of complex formation in case of CMC- $\text{Fe}(\text{NO}_3)_3$ ($\log k = 5.648$) is higher than that prepared from FeCl_3 salt ($\log k = 5.505$) (13).

Figure (3) shows the variation of strength properties of wood pulp-CMC complex paper sheets with changing the cation of metal salt

TABLE IV Effect of FeCl₃ and polymer complexes addition on mechanical and dielectric properties of produced paper sheets

Additive	pH	Ash. %	Mechanical properties			Dielectric properties*	
			Breaking length, m	Burst factor	Tear factor	ε'	ε''
–	6.53	0.21	4539.35	33.07	108.07	3.68	0.84
FeCl ₃	6.65	7.42	5044.49	45.55	148.55	4.25	1.72
PVA-FeCl ₃ complex	6.36	3.92	4352.80	42.64	119.11	4.99	1.44
HEC-FeCl ₃ complex	7.08	8.92	4646.17	35.17	129.84	3.89	0.69
CMC-FeCl ₃ complex	6.36	10.40	6122.38	54.42	153.48	4.90	1.44
CMC-Fe(NO ₃) ₃ complex	7.32	7.69	6657.32	57.98	159.90	4.00	0.78
CMC-ZnCl ₂ complex	6.62	5.27	7049.34	60.42	136.12	4.99	0.97

*Dielectric properties at frequency 0.5 kHz.

(FeCl₃ & ZnCl₂) used for complex formation. It is clear that despite the amount of metal in case of CMC-Fe(III) complex addition (relatively high ash content; Tab. III-b) was greater than CMC-Zn(II) complex addition, the strength properties of produced paper sheets made from the former complex was lower than the latter complex. This observation is probably due to the type of combination of metallic ions in complex formation. Whereas, in case of Zn(II) ions the ionically bond is formed; while, chelated bond (covalent coordinated bond) is formed in case of Fe(III)-complex [21], consequently, the bridging of cellulose fibres through the metals of CMC-complexes also affect.

Dielectric Properties

Based on the results obtained from Figures (1–3), the paper sheets produced from wood pulp and polymer complexes, at neutral pH were subjected in this study. Whereas, the neutral pH of preparation process was suitable condition to produce sheets possess relatively high strength properties, compared with those produced from acidic and alkaline pH's.

Figures (4–6) show the variation of dielectric constant (ε') and dielectric loss (ε''), of untreated and polymer-complexes addition paper sheets with frequency at room temperature; ~25°C. It can be seen that for all samples under investigation the electrical properties

(ϵ' & ϵ'') decrease with the increase of frequency from 0.5–50 kHz. This decrease can be attributed to the dielectric dispersion occurring with the increased frequency, which results from the lag of molecules behind the alternation of the applied electric field [22].

The absorption curves relating ϵ'' and frequency indicate that there are some absorption regions which are expected to be at the lower frequency range. One of these regions could be due to either d.c. conductivity or/and Maxwell Wanger effect. The d.c. conductivity for the investigated samples was measured by the application of Ohm's law to direct current flaving through the samples at different voltages ranging between 0 and 150 volts. No pronounced current was detected, indicating that there is no d.c conductivity. It is sure also that this effect is not due to bad contact between the sample and condenser plates as the measurements were repeated with aluminum foil stuck on the two faces of the samples and no change in the results was noticed. In any case, this effect is particularly a Maxwell-Wagner effect which could be attributed to the difference in the conductivities and permittivities of the substances composing the prepared samples. Some result was found in case of some other polymers [23].

The variation with frequency of both the dielectric constant and dielectric loss for paper samples prepared from addition PVA-, HEC- and CMC-complexes with FeCl_3 is given in Figure 4. Electrical properties of paper sheets prepared from untreated and FeCl_3 addition wood pulps were taken for comparison. It can be seen that, the dielectric constant values obtained with FeCl_3 , PVA- FeCl_3 and CMC- FeCl_3 complexes at a given frequency were greater than that obtained from untreated wood pulp. The improvement in dielectric properties (ϵ' & ϵ'') in case of polymer complexes addition were higher than FeCl_3 addition paper sheets. The variation of electrical properties with changing the type of ligand polymer was greatly noticed at low frequency (0.5 kHz).

The increase of (ϵ') in the case of FeCl_3 addition paper sheets can be explained if we taken into consideration the polarization of the adsorbed ferric ions due to their displacement under the effect of the electric field (8). While, the increase in such property in case of polymer complexes addition is probably related to molecular polarization of side group of unchelated polymer (COO^- & OH), in addition to polarization of adsorbed (chelated) ferric ions.

It is clear also that (Fig. 4), controlling the oxidation of wood pulp paper sheets resulted from FeCl_3 addition through complex formation improves the electrical insulation (high ϵ' & low ϵ'') property of polymer complexes (PVA- & CMC- FeCl_3 complexes) paper sheets than that prepared from FeCl_3 addition.

For the case of HEC- FeCl_3 complex addition, it is clear that the electrical properties of produced paper sheets was relatively low than those made from wood pulp without additives, PVA- and CMC- FeCl_3 complexes addition. This mainly related to decrease the oscillation of polar hydroxyl groups of cellulose molecules rather than the polarization of adsorbed metal ions.

The increase of ϵ' of CMC-complex addition paper sheets than HEC-complex addition is related to the presence of unchelated carboxyl groups of CMC ligand (24), in addition to the presence of water molecules in complex (Tab. II). The presence of water molecules was estimated from micro-analytical analysis, IR- and electronic spectra measurements [13].

However, the increase in ϵ' of paper sheets produced from PVA- FeCl_3 complex addition than HEC- FeCl_3 addition is related to the less adsorption of Fe(III) on PVA as a result of its lack in carbonyl and carboxyl group [21], as manifested from the ash content in paper sheets (Tab. IV). Therefore, the number of oscillation of unchelated or weak hydrogen bonded hydroxyl groups in case of PVA-complex addition is relatively higher than HEC-complex addition sheets which has relatively high ash content.

The data obtained in Figure 5 showed that, the electrical properties of polymer complex-paper sheets were greatly influenced by the type of anion in ferric salt used for complex formation. Whereas, the use of CMC complex with FeCl_3 greatly improves the ϵ' of produced sheets, compared with CMC complex with $\text{Fe}(\text{NO}_3)_3$ salt. These results reverse to some extent the results of mechanical properties (Fig. 2). The greater strength properties of produced paper sheets from CMC-complex addition with $\text{Fe}(\text{NO}_3)_3$ refer to higher bonded OH groups of cellulose pulps, consequently, less oscillation and polarizability of OH groups occur.

For the effect of cation of metal salt of polymer complex, Figure (6) shows that the dielectric properties of paper produced from addition of CMC-complex with ZnCl_2 was greatly higher than those produced

from complex of CMC with FeCl_3 . Both type of complexes produced relatively high insulating paper than paper made from untreated wood pulp. The results obtained are probably attributed to the ash content of produced paper sheets; whereas, the amount of chelated metallic ions was directly related to the electrical charge of ions; $\text{Fe}^{3+} > \text{Zn}^{2+}$. Therefore, relatively high carboxyl group of unchelated CMC ligand exists in case of Zn(II)-complex than Fe(III)-complex, consequently, the increase in dielectric constant was noticed.

On the other hand, the above observation is probably due to the change of the type of combination between metal and cellulose. Whereas, in case of Zn^{2+} the ionic bond is formed; while chelated (covalent coordinated) bond is formed in case of Fe^{3+} [21].

For comparing the values of dielectric properties of polymer-complexes addition paper sheets (Figs. 4–6), it could be concluded that the best insulating paper sheets was obtained from CMC- ZnCl_2 complex addition.

Infra-Red Spectra Measurements

The main infra-red absorption bands and the IR-measurements of wood pulp, wood pulp- FeCl_3 addition and wood pulp-polymer complexes addition paper sheets are registered in Tables V & VI. The relative absorbance of band was calculated as the ratio of the absorbance at the subscript wave-number to the absorbance of the wave-number at $\sim 1328 \text{ cm}^{-1}$, which corresponds of CH rocking of ring. The asymmetry index was defined as the ratio of the band widths, at $4000\text{--}3000 \text{ cm}^{-1}$ region, on the low and the high frequency side of the maximum at half band absorbance; the bonded hydroxyl stretching gives unsymmetrical band with broadening towards the lower frequency sides [25]. The mean strength of the H-bonds (MHBS) was calculated as the ratio $A_{\text{OH}}/A_{\text{CH}}$, where A is the absorption of the stretching vibration of subscript group [25]. The crystallinity index is the ratio of the absorption of band at 1430 cm^{-1} to the band at 900 cm^{-1} [26].

The results in Tables V & VI show that paper sheets produced either from addition of FeCl_3 or polymer complexes result in increased the asymmetry index, MHBS, and crystallinity index; while,

TABLE V Main IR-absorption bands of wood pulp-polymer complexes paper sheets

Type of Additive	ν_{OH} stretching		$\nu_{C=O}$ stretching		ν_{OH} bending		ν_{CH} bending		ν_{CH} rocking	
	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E
O ₂	3853	0.51								
FeCl ₃	3421	1.66	2916	1.06	1637	0.74	1428	0.98	1369	1.02
PVA-FeCl ₃ complex	3421	1.29	2902	0.90	1644	0.83	1438	0.97	1373	1.04
HEC-FeCl ₃ complex	3421	1.45	2900	0.94	1637	0.79	1431	0.99	1373	1.05
CMC-FeCl ₃ complex	3421	1.51	2918	0.90	1637	0.69	1431	0.98	1375	1.05
CMC-Fe(NO ₃) ₃ complex	3411	1.62	2918	1.08	1650	0.89	1425	1.00	1380	1.05
CMC-ZnCl ₂ complex	3384	1.54	2902	0.96	1637	0.85	1428	1.01	1375	1.04
					1637	0.75	1425	0.98	1373	1.02
									894	1.03
									900	0.81
									900	0.83
									900	0.84
									900	0.93
									900	0.83
									900	0.61

$E = \frac{A_{\nu}}{A_{1328\text{cm}^{-1}}}$; A_ν: absorbance at the subscript wave number, and A_{1328cm⁻¹}: absorbance at the wave number 1328 cm⁻¹.

TABLE VI IR-measurement of wood pulp-polymer complexes paper sheets

Type of additive	A_{OH} max.	Asymmetry Index	MHBS	Cryst. Index
			$\frac{A_{OH}}{A_{CH}}$	$\frac{A_{1430\text{cm}^{-1}}}{A_{900\text{cm}^{-1}}}$
—	3421	1.391	1.227	0.944
FeCl ₃	3421	1.495	1.849	1.198
PVA-FeCl ₃ complex	3421	1.609	1.494	1.087
HEC-FeCl ₃ complex	3421	1.782	1.679	1.164
CMC-FeCl ₃ complex	3421	1.609	1.663	1.197
CMC-Fe(NO ₃) ₃ complex	3411	1.870	1.494	1.216
CMC-ZnCl ₂ complex	3384.46	1.357	1.605	1.603

the shift of maximum absorption band of stretching vibration of OH groups (A_{OH} max.) to lower wave-number was only observed in case of complexes of CMC with Fe(NO₃)₃ and ZnCl₂.

The broadening of the band (Asymm. Index > 1;1.39), in the region of the wave-number 4000–3000 cm⁻¹, of wood pulp paper sheets without additives reveals that the hydroxyl groups are not free but entering into different modes of hydrogen bonds [27]. On FeCl₃ addition, the increase of asymmetry index is related to destruction of weak hydrogen bonds, of cellulose pulp, by oxidation and subsequent re-ordering of the chains with the formation of new stronger hydrogen bonds [8], during sheet formation process. Therefore, the MHBS and crystallinity index also increase. Due to oxidation of some hydroxyl groups of wood pulp adsorbed ferric ions to carbonyl or carboxyl, the increase in relative absorbance bands corresponding to stretching vibration of C=O group and in-plane bending vibration of C—OH of carboxyl group was noticed, compared to untreated sheets.

For the case of complex addition, the broadening of hydroxyl group bands to relatively low wave-number, compared to untreated paper sheets is probably related to bridging the hydroxyl groups of wood pulp through multivalent metal ions in complex sphere. However, due to the competition of the metal cations for electrons of which the bonds are composed between two hydroxyl groups, and due to controlling the oxidation of wood pulp hydroxyl groups, as a results of chelated Fe(III) ions with polymer, the MHBS of polymer complex addition is less than FeCl₃ addition paper sheets. Whereas, the MHBS refers to the number of hydroxyl groups of cellulose pulp entering the hydrogen bonds [25].

It is evident from Table VI that the position of the OH band maximum of paper sheets shifted to lower wave-number on adding CMC-complexes with $\text{Fe}(\text{NO}_3)_3$ and ZnCl_2 , indicating that stronger bonded OH groups are formed. According to Badger and Bauer [28], the magnitude of the shift in OH fundamental due to hydrogen bonding could be used as a measure of the strength of hydrogen bonds formed; therefore, the bonds formed on CMC-Zn(II) complex addition is higher than CMC-Fe(III) of $\text{Fe}(\text{NO}_3)_3$ complex addition. Due to this reason the strength properties of added the former complex paper sheets is higher than latter ones (Tab. IV).

On comparing the results obtained for IR-measurements (Tab. VI) with that obtained from electrical properties measurements (Tab. IV & Figs. 4–6), of polymer complexes addition paper sheets it is clear that, the increase of the electrical properties accompanied the decrease of crystallinity index in case of paper sheets produced from addition of HEC- FeCl_3 , CMC- FeCl_3 and CMC- $\text{Fe}(\text{NO}_3)_3$ complexes. However, the reverse was noticed in case of PVA- FeCl_3 and CMC- ZnCl_2 complexes addition. This is probably due to the amount of chelated metal ions [Fe(III) or Zn(II)], as clear from the values of ash content (Tab. IV), consequently, the number of molecular polymerization of side groups; hydroxyl and carboxyl groups, in ligand polymers increases.

From the above results it could be concluded that, the addition of polymer complexes to wood pulp during beating process was successful for producing new insulating paper sheets with high strength properties.

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