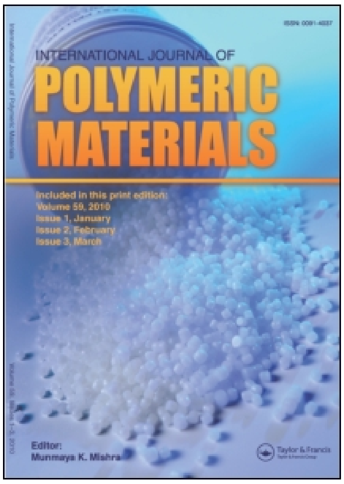

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Spectral and Thermal Analyses of a Novel Cellulose Derivative "Propionic Acid Hydrazide-3-(OCellulose)" and its Combination with some Metal Ions

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The new cellulose derivative containing nitrogen "Propionic Acid Hydrazide-3-(OCellulose)" was prepared from bleached kraft bagasse pulp *via* the formation of methyl propionate-3-(OCellulose), [MPC]. Different reaction variables were applied during the formation of [MPC], such as : sodium hydroxide concentration, sodium hydroxide to cellulose ratio, time and temperature of reaction. On the basis of the results from IR-absorption spectra the optimum conditions of the formation of [MPC] by Michael addition reaction were determined. The prepared Propionic Acid-Hydrazide-3-(OCellulose); [PAHC], and its combination with some metal ions were characterized by FTIR-spectra, micro-analyses and thermal analysis.

The thermal properties were evaluated by non-isothermal TGA and the activation energies of the degradation of the samples were calculated using the Coats and Redfern equation.

Keywords: Novel cellulose derivative; cellulose derivative containing nitrogen; cellulose derivative-metal ions combination; spectra analysis; thermal stability of modified pulp

INTRODUCTION

Cellulose can be used in certain cases to collect metal ions, particularly when organic solvents are used [1]. Modified cellulose can collect metal

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*Corresponding author. e-mail: altafhbm@frcu.eun.eg ions from solutions much more effectively than natural cellulose [2]. Therefore, attempts to attach carboxyl groups, phosphate and nitrogen and/or sulfur containing groups to the backbone of cellulose have been carried out by many authors [3 – 13].

Within the framework of preparation the cellulose derivative containing nitrogen, the numerous procedures were discovered, including cyanoethylation of cellulose [4], amidoximation and carbamylethylation of cyanoethylated cellulose [5, 6 and 14], nitration of carboxymethyl cellulose ether [15], graft polymerization with nitrogen containing monomer, *e.g.*, acrylonitrile and acrylamide [16 – 18], and chemical introduction of organic amines to cellulose *via* 6-chloro-6-deoxycellulose or 2,3-Dibromopropyl cellulose [19 – 21].

In this work, a new cellulose derivative containing nitrogen groups "Propionic Acid Hydrazide-3-(OCellulose)" was prepared *via* methyl propionate-3-(OCellulose), using hydrazine hydrate. The formation of [MPC] under different experimental conditions was confirmed by FTIR-spectra technique. The FTIR-spectra, micro-analyses and thermal stability of the prepared [PAHC] and its combination with metal ions were also studied.

EXPERIMENTAL

Materials

- Bleached kraft bagasse pulp was used as cellulose material. The unbleached pulp was supplied by Edfu-Mill Upper Egypt. The conventional four stages bleaching method (chlorination, soda, hypochloride and chlorite steps) were used in this study. The bleached pulp was chemically analyzed as α-cellulose [22], pentosans [23], lignin [24] and ash.
- Pure grades sodium hydroxide
- Analar solutions of hydrazine hydrate and dimethyl sulfoxide.
- Methyl acrylate was purified by conventional methods.
- Analytical grades of $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $MnCl_2 \cdot H_2O$, $MgCl_2$ and $CdCl_2$ were used for preparing a solutions of metal ions.

Preparation of Propionic Acid Hydrazide-3-(OCellulose) [PAHC]

The formation of propionic acid hydrazide-3-(OCellulose) from bleached kraft bagasse pulp was carried out by a 2-stages method;

Formation of Methyl Propionate-3-(OCelluose) [MPC]

Michael addition reaction by using methyl acrylate was used for preparation of methyl propionate-3-(OCellulose). In this stage the bagasse pulp (1 gm oven dry pulp) was immersed in 20 ml. of 5, 10, 15 and 20% (wt./vol.) sodium hydroxide solution for one hr. at room temperature ~18–20°C. The formed alkali cellulose was filtered under suction using a sintered glass funnel and pressed with a glass rod until the desired ratios of cellulose to sodium hydroxide solution were obtained, namley : 1 : 2, 1 : 5, 1 : 10 and 1 : 15 (wt./wt.). Purified methyl acrylate was added to the formed alkali cellulose in ratio 3 : 1, and allowed to stand, with occasionally shaking, at 30°C, 50°C and 65°C for a desired period (0.5–4 hrs.). At the end of reaction time the product [MPC] was neutralized by 10% acetic acid, then washed thoroughly with bidistilled water and dried in a vacuum oven at 40°C.

Formation of Propionic Acid Hydrazide-3-(OCellulose) [PAHC]

The prepared methyl propionate-3-(OCellulose) was suspended in DMSO and excess hydrazine hydrate was added. The mixture was allowed to stand at 90°C for 2 hrs. The mixture was also filtered, washed by bidistilled water till neutrality, and dried in vacuo. The degree of substitution (D.S.) of the prepared [PAHC] was determined from the percent of nitrogen content in sample.

Combination of Cellulose Derivative with Metal Ions

Aqueous solutions of bidistilled water containing 0.1 M of trivalent and divalent metal chlorides such as $FeCl_3$, $CrCl_3$, $CuCl_2$, $NiCl_2$, $MnCl_2$, $MgCl_2$ and $CdCl_2$, were prepared. The [PAHC] powder (0.5 g) was put into a glass bottle containing 50 mls. of the metal chloride solution. The mixture was gently stirred for 24 hrs. at room temperature 18–20°C. PAHC-metal product was filtered off, and the amount of metal ions combined with cellulose derivatives was determined from the atomic absorption of the remaining metal solution.

Analysis

Infra-red Absorption Spectra

The IR-spectra were recorded with the Insco FT/IR-300E, Fourier Transform Infrared Spectrometer at 4000–200 cm^{-1} wavelength, using samples in the form of KBr tables.

For the spectrophotometric measurements, the degree of crystallinity of the samples was determined from the relation [25],

$$C_rD = \frac{A_{1429\,\text{cm}^{-1}}}{A_{900\,\text{cm}^{-1}}}$$

the mean strength of the hydrogen bond [26],

$$\text{MHBS} = \frac{A_{\text{OH(str.)}}}{A_{\text{CH(str.)}}}$$

where A is the absorption of the stretching vibration of subscript group, and the mercerization depth from [25]

$$M_D = \frac{A_{1375\,\text{cm}^{-1}}}{A_{1325\,\text{cm}^{-1}}}$$

Micro-analyses

Carbon, hydrogen, and nitrogen contents were determined by the Micro-analytical Unit of Cairo Unversity.

Thermal Analysis

Thermogravimetric analysis (TG and DTG) of the investigated samples was done using PERKIN ELMER (Thermogravimetric Analyzer

TGA 7). Analysis was performed with a heating rate of 10°/minute and flow rate 50 cc/minute, under nonisothermal condition, in the presence of nitrogen.

Procedure of TGA Curve Analysis

The determination of kinetic parameters (activation energy, E_a, and frequency factor, A) from weight loss *versus* temperature data can be carried out by using Coats and Redfern Equation [27]. 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 K min^{-1}), R is the gas constant (in kJ mol^{-1} K^{-1}) and T is the temperature (in K) and A the frequency factor (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 various of n, should give a straight line with the most appropriate values [28]. Thus, the method of least square is applied for the equation, taking values of n ranging from 0 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 degradation process. The E_a and A were calculated from the slope and intercept, respectively.

RESULTS AND DISCUSSION

The chemical analyses of the bleached kraft bagasse pulp used in this study, and alkali treated bagasse pulp are given in Table I.

FTIR-spectra

Modified Kraft Bagasse Pulp

IR-spectrophotometric technique used here as a tool to confirm the formation of methy propionate-3-(OCellulose) by Michael addition

TABLE I Chemical analysis of untreated and alkali treated bleached bagasse pulps

Analysis	*Untreated pulp*	*Alkali treated pulp*			
		5%*NaOH*	10%*NaOH*	15%1*NaOH*	20%*NaOH*
α-Cellulose, %	77.60	78.00	78.40	79.80	80.20
Pentosans, %	20.70	20.65	19.04	18.30	18.40
Lignin, %	0.67	–	–	–	–
Ash, %	0.43	0.416	0.411	0.43	0.404

reaction, as a first step to the formation of propionic acid hydrazide-3-(OCellulose). To clarify the variation of the relative absorbencies of some functional groups, *e.g.*, OH, CH, and C=O, in addition to the crystallinity index as a result of Michael addition reaction, the relative absorbencies of such groups and crystallinity indices of bagasse pulp treated by the same conditions of the formation of alkali cellulose (during Michael addition reaction), followed by solvent exchange to isolate the alkali and maintain the degree of decrystallization as the case of alkali cellulose [29], were also measured for comparison.

The relative absorbency, *E*, is the ratio of the absorbency of the investigated band to the band at 1160 cm^{-1} which corresponds to the ring frequency (nearly constant for all samples).

Table II shows the main IR-frequencies, relative absorbencies and crystallinity indices of untreated and alkali treated bleached kraft bagasse pulp; while (Tabs. III–VII) show those values obtained from Michael addition reaction of bleached pulp under different experimental conditions.

TABLE II Main IR-frequencies bands and IR-measurements of untreated and alkali treated bagasse pulps

Untreated		5%*NaOH*		10%*NaOH*		15%*NaOH*		20%*NaOH*	
ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*
3421.1	1.147	3384	1.168	3417	1.150	3442	1.135	3446	1.078
2900	0.336	2900	0.727	2900	0.738	2900	0.745	2900	0.775
1640	0.641	1637	0.614	1637	0.665	1637	0.644	1637	0.659
1430	0.766	1430	0.720	1430	0.797	1430	0.732	1430	0.757
1375	0.798	1373	0.762	1373	0.839	1373	0.784	1373	0.819
1060	1.155	1059	1.226	1059	1.150	1061	1.188	1061	1.155
900	0.609	900	0.589	900	0.685	900	0.651	900	0.703
MHBS	1.545	MHBS	1.607	MHBS	1.558	MHBS	1.524	MHBS	1.390
C_rD	1.258	C_rD	1.222	C_rD	1.163	C_rD	1.125	C_rD	1.078
M_D	–	M_D	1.026	M_D	1.160	M_D	1.130	M_D	1.146

TABLE III Main IR-frequencies bands and IR-measurements of mehtyl propionate-3-(OCellulose) prepared at 30°C, for different periods

0.5 *hr.*		1 *hr.*		2 *hrs.*		3 *hrs.*		4 *hrs.*	
ν, cm^{-1}	E	ν, cm^{-1}	E	ν, cm^{-1}	E	ν, cm^{-1}	E	ν, cm^{-1}	E
3421	1.211	3421	1.186	2421	1.217	3421	1.180	3421	1.148
2900	0.949	2902	0.844	2900	0.899	2902	0.848	2902	0.817
1640	0.855	1640	0.795	1640	0.869	1640	0.713	1640	0.677
1560	0.901	1560	0.931	1560	0.961	1560	0.709	1560	0.578
1430	0.915	1329	0.889	1430	0.907	1430	0.822	1430	0.795
1375	0.906	1363	0.863	1365	0.886	1373	0.835	1380	0.817
1060	1.109	1060	1.175	1060	1.136	1060	1.158	1059	1.162
900	0.755	900	0.673	900	0.716	900	0.687	900	0.677
840	0.669	840	0.618	840	0.662	840	0.581	840	–
MHBS	1.277	MHBS	1.406	MHBS	1.355	MHBS	1.391	MHBS	1.405
C_rD	1.210	C_rD	1.321	C_rD	1.266	C_rD	1.196	C_rD	1.174

Constant conditions: NaOH, %5, NaOH/pulp after pressing: 2/1 and methyl acrylate/pulp:3/1.

TABLE IV Main IR-frequencies bands and IR-measurements of methyl propionate-3-(OCellulose) prepared at 50°C, for different periods

0.5 *hr.*		1 *hr.*		2 *hrs.*		3 *hrs.*		4 *hrs.*	
ν, cm^{-1}	E	ν, cm^{-1}	E	ν, cm^{-1}	E	ν, cm^{-1}	E	ν, cm^{-1}	E
3421	1.170	3421	1.148	3421	1.205	3356	1.130	3382	1.092
2900	0.855	2900	0.821	2902	0.810	2902	0.875	2900	0.811
1640	0.707	1640	0.746	1640	0.770	1640	0.812	1640	0.577
1560	0.697	1560	0.770	1560	0.805	1560	0.843	1560	0.613
1430	0.835	1431	0.848	1430	0.866	1430	0.880	1430	0.808
1375	0.851	1375	0.825	1375	0.851	1375	0.867	1373	0.811
1059	1.140	1060	1.171	1050	1.177	1060	1.142	1059	1.172
900	0.716	900	0.664	900	0.671	900	0.629	900	0.658
–	–	840	0.556	840	0.522	840	0.628	840	0.531
MHBS	1.369	MHBS	1.399	MHBS	1.488	MHBS	1.366	MHBS	1.346
C_rD	1.174	C_rD	1.278	C_rD	1.29	C_rD	1.40	C_rD	1.227

Constant conditions: NaOH, %5, NaOH/pulp after pressing: 2/1 and methyl acrylate/pulp: 3/1.

From Tables II–VII it is clear that the curves of the IR-spectra are characterized by the following bands:

- The broadening of the bands in the region of the wave-number 4000–3000 cm^{-1} reveals that the hydroxyl groups are not free but enter into different modes of hydrogen bonds, and are characterized for the polymeric association. On Michael addition reaction,

TABLE V Main IR-frequencies bands and IR-measurements of methyl propionate-3-(OCellulose) prepared at 65°C, for different periods

0.5 *hr.*		1 *hr.*		2 *hrs.*		3 *hrs.*		4 *hrs.*	
ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*
3384	1.038	3421	1.189	3385	1.038	3384	1.128	3421	1.145
2900	0.726	2900	0.814	2900	0.726	2900	0.756	2900	0.833
1640	0.644	1640	0.692	1640	0.644	1640	0.671	1640	0.697
1560	0.707	1560	0.692	1560	0.707	1560	0.629	1560	0.645
1430	0.809	1430	0.810	1430	0.809	1431	0.792	1430	0.823
1363	0.787	1375	0.822	1363	0.787	1375	0.788	1373	0.838
1060	1.234	1060	1.182	1060	1.234	1058	1.193	1060	1.154
900	0.559	900	0.559	900	0.663	900	0.629	900	0.701
840	0.444	840	0.548	840	0.444	840	0.512	–	–
MHBS	1.428	MHBS	1.461	MHBS	1.428	MHBS	1.491	MHBS	1.374
C_rD	1.449	C_rD	1.449	C_rD	1.22	C_rD	1.260	C_rD	1.175

Constant conditions: NaOH, %5, NaOH/pulp after pressing: 2/1 and methyl acrylate/pulp: 3/1.

TABLE VI Main IR-frequencies bands and IR-measurements of methyl propionate-3-(OCellulose) prepared from different concentrations of sodium hydroxide

0%*NaOH*		5%*NaOH*		10%*NaOH*		15%*NaOH*		20%*NaOH*	
ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*
3420	1.151	3356	1.130	3385	1.106	3442	1.137	3446	1.172
2900	0.735	2902	0.875	2902	0.786	2900	0.867	2900	0.845
1640	0.597	1640	0.812	1640	0.826	1640	0.777	1640	0.791
–	–	1560	0.843	1560	1.017	1560	0.851	1560	0.869
1430	0.747	1430	0.880	1430	0.916	1430	0.875	1430	0.873
1373	0.785	1375	0.867	1363	0.870	1370	0.875	1373	0.873
1060	1.181	1059	1.142	1060	1.207	1060	1.136	1060	1.147
900	0.597	900	0.629	900	0.579	900	0.693	900	0.681
–	–	840	0.628	840	0.647	840	0.588	840	0.576
MHBS	1.566	MHBS	1.366	MHBS	1.535	MHBS	1.311	MHBS	1.387
C_rD	1.250	C_rD	1.40	C_rD	1.581	C_rD	1.269	C_rD	1.283

Constant conditions: NaOH/pulp after pressing: 2/1 methyl acrylate/pulp:3/1 and Temp. of Michael addition Rx.: 50°C for 3 hrs.

the maximum absorption band of some samples is shifted to a lower wave-number comparing with alkali treated samples, indicating the substitution of OH groups by acrylate groups. Also, the crystallinity indices of methyl propionate-3-(OCellulose) are relatively higher than those of alkali treated samples, which indicate the formation of a higher state of order.

- In the absorption region 3000 – 2800 cm^{-1}, characteristic bands due to the stretching vibration of CH_2 groups are shown in the all

TABLE VII Main IR-frequencies bands and IR-measurements of methyl propionate-3-(OCellulose) prepared from different sodium hydroxide to pulp ratios

0*		2/1		5/1		10/1		15/1	
ν, cm^{-1}	E	ν, cm^{-1}	E	ν, cm^{-1}	E	ν, cm^{-1}	E	ν, cm^{-1}	E
3384	1.168	3356	1.297	3406	1.182	3421	1.202	3384	1.041
2900	0.727	2900	0.875	2902	0.753	2900	0.786	2900	0.673
1637	0.614	1640	0.812	1640	0.686	1640	0.606	1640	0.493
–	–	1560	0.843	1560	0.744	1560	0.532	1560	0.449
1430	0.720	1430	0.880	1429	0.825	1430	0.777	1430	0.673
1373	0.762	1375	0.867	1363	0.803	1375	0.805	1373	0.691
1059	1.226	1060	1.142	1058	1.401	1060	1.073	1058	1.105
900	0.589	900	0.629	900	0.63	900	0.588	900	0.533
–	–	840	0.628	840	0.449	–	–	–	–
MHBS	1.607	MHBS	1.366	MHBS	1.571	MHBS	1.529	MHBS	1.547
C_rD	1.222	C_rD	1.40	C_rD	1.309	C_rD	1.321	C_rD	1.261

Constant conditions: NaOH, %: 5, methyl acrylate/pulp: 3/1 and Temp. of Michael addition Rx.: 50°C for 3 hrs.

*Alkali treated bleached bagasse pulp with 5% NaOH.

spectra. The relative absorbency, E, of this band increased in the case of [MPC] compared with alkali treated pulp, indicating the presence of acrylate groups in cellulose backbone.

- In the region of carbonyl groups 1700–1500 cm^{-1}, it is clear that for untreated and alkali treated bleached pulp one band was seen at 1637–1640 cm^{-1}, which is related to the C=C of residual lignin and/or C=O of aldehydic group of cellulose; while for the [MPC] samples, in addition to the band at $\sim$1640 cm^{-1}, a new band is appeared at 1560 cm^{-1}, this band corresponding to the carbonyl of acrylate groups. The relative absorbencies of these bands changed with changing the conditions of the preparation of [MPC].
- Bands shown in the range of 1500–1400 cm^{-1} and those at 900 cm^{-1} and 840 cm^{-1} are assigned to CH_2-bending and CH_2-rocking vibration, respectively. On Michael addition reaction of bleached bagasse pulp, the relative absorbency, E, of the first band at $\sim$ 1430 cm^{-1} increased; while for the second band, at 900–800 cm^{-1}, nearly no change in most samples in observed. The appearance of a new band in the spectra of [MPC] indicates the presence of methyl acrylate group in the modified pulp.
- The association band in alcohol's at $\sim$ 1060 cm^{-1}, which caused by stretching vibration of the C—O, is shown in the spectra of untreated,

alkali treated and modified pulps. No relation between the relative absorbency of this band and the change in the conditions of the Michael reaction is noticed.

The above results confirm the formation of methyl propionate-3-(OCellulose).

From Figures 1 and 2, which clear the relation between the relative absorbencies of the bands of acrylate group at 1560 cm^{-1}, 1430 cm^{-1} and 840 cm^{-1}, in addition to the crystallinity index as a function of time, temperature, alkali concentration and alkali to pulp ratio, it can

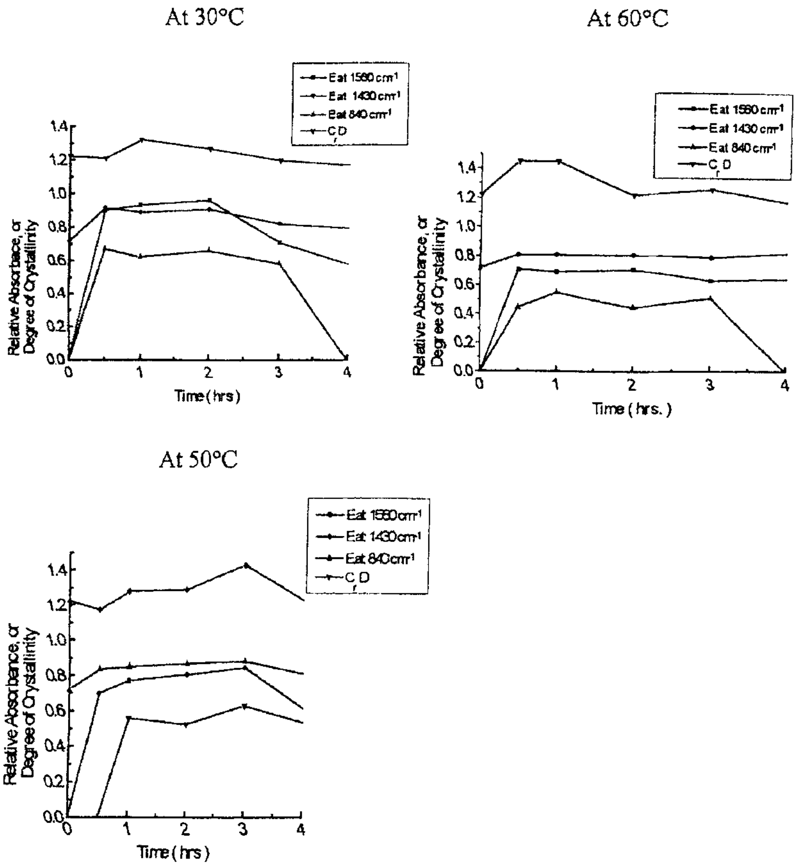
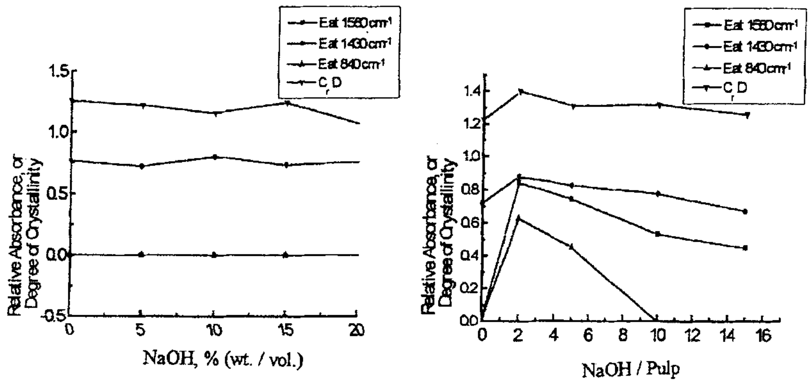


FIGURE 1 Effect of time of Michael addition reaction at different temps. on the relative absorbances of some characteristic bands and the degree of crystallinity.


Without Michael Addition

Liquor ratio

Michael Addition

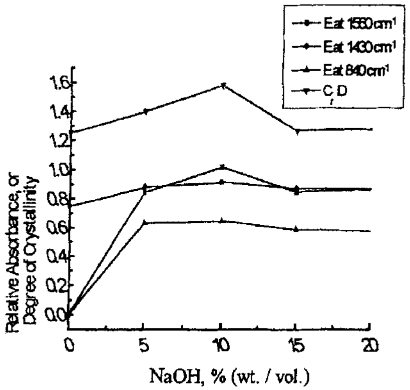


FIGURE 2 Effect of NaOH and NaOH/pulp ratio of Michael addition reaction on the relative absorbances of some characteristic bands and the degree of crystallinity.

be concluded that, the optimum conditions to prepare [MPC] are: 10% alkali concentration and 2 NaOH/pulp, for 3 hrs. at 50°C. This is probably related to relatively increase of the mercerization depth (M_D) of alkali cellulose (Tab. II), which assigned the maximum structure change in cellulose sample [25].

Table VIII shows the main IR-frequencies and their relative absorbencies of prepared propionic acid hydrazide-3-(OCellulose); N% 4.4 and D.S. 0.29. The [PAHC] was prepared from treating the

TABLE VIII Main IR-frequencies bands and IR-measurements of the prepared propionic acid hydrazide-3-(OCellulose) and its combination with some metal ions

[PAHC]		*[PAHC]-Fe(III)*		*[PAHC]-Cr(III)*		*[PAHC]-Cu(II)*		*[PAHC]-Ni(II)*		*[PAHC]-Cd(II)*		*[PAHC]-Mg(II)*		*[PAHC]-Mn(II)*	
ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*	ν, cm^{-1}	*E*
3415	1.108	3383	1.006	3421	1.285	3356	1.180	3385	1.136	3419	1.127	3417	1.180	3384	1.247
2900	0.805	2902	0.795	2902	0.827	2902	0.762	2902	0.769	2902	0.783	2902	0.862	2902	0.854
1615	0.940	1637	0.843	1617	0.667	1615	0.651	1617	0.647	1615	0.747	1615	0.769	1617	0.740
1430	0.796	1430	0.743	1430	0.727	1430	0.7324	1430	0.749	1430	0.813	1430	0.835	1430	0.787
1370	0.821	1373	0.782	1373	0.762	1373	0.770	1373	0.777	1370	0.831	1375	0.857	1370	0.802
1059	1.153	1058	1.108	1059	1.198	1059	1.206	1059	1.182	1058	1.163	1059	1.135	1059	1.176
900	0.697	900	0.626	900	0.598	900	0.621	900	0.625	900	0.704	900	0.727	900	0.648
617	0.844	617	0.845	617	0.826	617	0.832	617	0.823	617	0.877	617	0.888	617	0.850
345	0.751	350	0.712	350	0.706	350	0.723	350	0.71	350	0.812	350	0.832	350	0.758
–	–	281	1.099	231	1.672	235	1.032	233	1.080	233	1.371	235	1.394	237	1.210
MHBS	1.377	MHBS	1.475	MHBS	1.554	MHBS	1.550	MHBS	1.484	MHBS	1.439	MHBS	1.368	MHBS	1.460
C_rD	1.142	C_rD	1.186	C_rD	1.215	C_rD	1.180	C_rD	1.198	C_rD	1.155	C_rD	1.149	C_rD	1.214

prementioned prepared [MPC], under optimum Michael reaction conditions, with hydrazine hydrate.

By comparing the relative absorbenceis of the bands in the spectrum of [PAHC]; Table VIII, with those of spectrum of [MPC]; Table IV, it is clear that, the band maximum corresponding to stretching vibration of OH group was shifted to higher wave-number, and the relative absorbencies of the bands characteristic to OH- and CH-stretching vibrations (at 3415 and 2900 cm^{-1}, respectively), and CH- rocking vibration (at ~900 cm^{-1}) increased. This is related to the introducing of hydrazide groups in cellulose backbone.

The spectrum of [PAHC] also shows that, in the region of 1700–1500 cm^{-1} one broad band only appeared at 1615 cm^{-1}. This characteristic to the stretching vibration of C=O of aldehyde group of cellulose and propionic acid hydrazide group. The relative absorbency of this band also increased compared with the band at 1640 cm^{-1} of [MPC].

For the degree of crystallinity it is clear that, the degree of crystallinity of [PAHC] is lower than [MPC], this is related to the alkaline hydrolysis effect of hydrazine hydrane on cellulose pulp.

Propionic Acid Hydrazide-3-(OCellulose)-metallic Ion Samples

From Table VIII it is clear that, the treatment of propionic acid-3-(OCellulose) with Fe(III), Cu(III), Ni(II) and Mn(II) salts leads to shift the band maximum corresponding to stretching vibration of OH or NH groups of [PAHC] to lower wave-number, this indicates the chelate bond is formed and the involvement of NH and residual hydroxyl groups of modified bagasse pulp in chelation with metal ions. However, the reverse was expected in the case of other metal ions Cr(III), Cd(II) and Mg(II); whereas no change in the band position is observed.

The IR-spectra of all [PAHC]- metal ions samples, except [PAHC]-Fe(III) spectrum, show that, the metallic ions undergo coordinate chelation with carbonyl oxygen in propionic acid hydrazide groups of modified pulp, whereas the decrease in the relative absorbencies corresponding to this group at 1615 cm^{-1} is observed. In other word, the combination of metallic ions with [PAHC] minimize the double bonding character of the carbonyl group. While, for the case of [PAHC]-Fe(III) sample, the relatively increase in the, *E*, of C=O group, in addition to the blue shift of the band position from $1615\,cm^{-1}$ to $1637\,cm^{-1}$, compared with other combined metallic samples, is probably related to the oxidation effect of $FeCl_3$ to the residual hydroxyl groups of cellulose [30, 31]. The appearance of a new band at $233.3\,cm^{-1}$ for the spectra of all [PAHC]-metallic ions samples confirms the present of M—O chelate bonds [32].

For the band corresponding to stretching vibration of CH at $\sim 2902\,cm^{-1}$ it is clear that, for all samples under investigation the band width decreased compared with the spectrum of [PAHC]. This may be related to reduce the space between cellulose chains as a result of combined metal ions. The relative absorbency of this band decreased in the case of [PAHC]-Fe(III), [PAHC]-Cu(II) and [PAHC]-Ni(II) samples.

Elemental Analyses of [PAHC]-metal Ion Samples

Table IX shows the elemental analyses (C, H and N%) of the prepared [PAHC] and its combination with some metallic ions. The amount of combined metal ions (mmol/1 g sample), in addition to the calculated percentages of coordinated water and the ratio of the number of metal atoms to number of PAH groups to number of glucopyranose units were also registered in Table IX.

Based on the results of IR-spectra of combined [PAHC] with metalic ions (Tab. VIII), and the results obtained in Table IX, we can be expected that, the propionic acid hydrazide group acts as a bidentate ligand, through NH_2 and C=O groups, during Fe(III) and Ni(II) ions combined with [PAHC]; While it is act as a monodentate ligand through the coordinate chelation with carbonyl of PAH-group in the case of Cr(III), Cd(II) and Mn(II) combined metallic ions. For the case of [PAHC]-Cu(II) and [PAHC]-Mg(II) samples, the PAH-group of some substituted glucopyranose unit acts as a bidentate and in the another unit acts as a monodentate ligand.

It is clear also that, the chelate bond is not only the propionic acid hydrazide group but also the hydroxyl of unsubstituted glucopyranose unit, as the case of combined [PAHC] with Fe(III) ion.

TABLE IX Elemental analyses and the amount of combined metal ions in propionic acid hydrazide-3-(OCellulose)

Sample	*C, %*	*H, %*	*N, %*	*Metal mmol/g [PAHC]*	*Coordinated H_2O, %**	*M : PAH-gps : Glucopy. Units*		
[PAHC]	44.10	2.80	4.40	–	–	–	–	–
[PAHC]-Fe(III)	40.10	3.05	4.40	1.78	4.6	8	7	24
[PAHC]-Cr(III)	42.05	3.10	4.20	0.93	3.65	17	30	100
[PAHC]-Cu(II)	41.10	2.60	4.10	1.25	–	4	5	18
[PAHC]-Ni(II)	40.3	2.60	4.02	1.60	–	3	3	10
[PAHC]-Cd(II)	43.5	2.80	4.30	0.13	–	1	12	40
[PAHC]-Mg(II)	43.0	3.70	4.30	1.07	9.00	2	3	10
[PAHC]-Mn(II)	42.4	2.7	4.23	0.73	–	10	21	72

* The present of coordinated water was calculated from the difference between calculated and found values of hydrogen percentages.

Thermal Analysis

Thermal Analysis of Modified Kraft Bagasse Pulp

The nonisothermal TG and DTG curves of bleached bagasse pulp and the prepared modified bagasse pulps [MPC and PAHC] are given in Figures 3–5.

Figure 6 represents the plot of $-r$ and SE as a function of n, for the decomposition stages of un-modified bleached pulp to calculate the appropriate order of degradation; while Figure 7 shows the relation between $\log_{10}[1-(1-\alpha)^{1-n}/T^2(1-n)]$ against $1/T$ of its degradation stages.

Table X summarize the temperature range, $-r$, SE, n, E_a, and A for each main degradation stages of un-treated, alkali treated and modified [MPC and PAHC] pulps.

The thermograms indicate that, the thermal decomposition of bagasse pulp (Fig. 3) is a multistage processes (5-stages). This is attributed to the removal of adsorbed water (1st-stage) and the decomposition of its components (lignin, hemicellulose and cellulose), stages 2–5 (main degradation stages), whereas the resitivity against thermal treatments follows the sequences : lignin > cellulose > hemicellulose [33].

For the case of methyl propionate-3-(OCellulose) samples which were prepared by Michael addition reaction using 5% and 10% NaOH to form alkali cellulose (Figs. 4 and 5), the main thermal degradation stages are reduced to 3 stages. This is related to the isolation of lignin and a part of hemicellulose during the step of formation of alkali cellulose, as manifested from Table I and the thermograms of alkali treated bagasse pulp under the same conditions of the formation of alkali cellulose. The additional decomposition stage in the case of [MPC]; 3 stages, than the case of alkali treated pulp; 2 stages, this may be assigned to the breakdown of acrylate groups in cellulose chains.

Table X shows that, generally the total activation energies, ΣE_a, of [MPC] samples are higher than alkali treated pulps. The thermal stability in the case of prepared [MPC] by using 10% NaOH is more pronounced than the case of using 5% NaOH. This may be related to relatively increase the structure changes (relatively high M_D; Tab. II) of pulp treated with 10% NaOH, and consequently more uniform

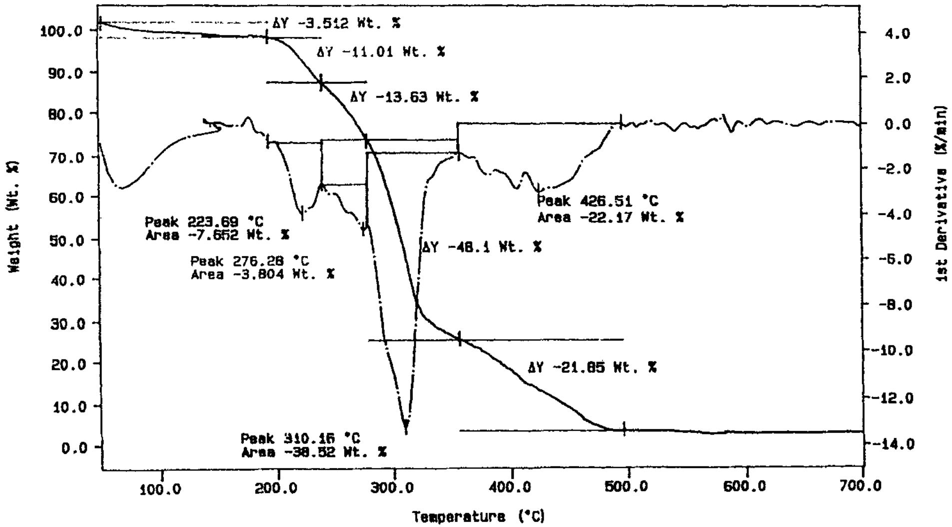
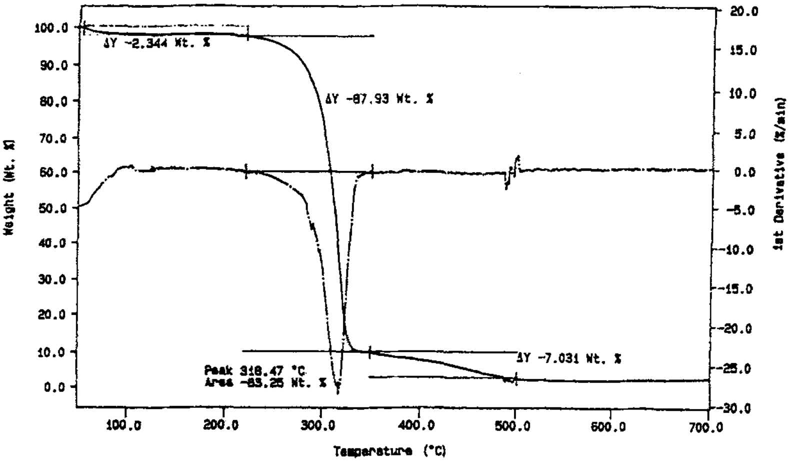


FIGURE 3 TG and DTA thermograms for untreated bagasse pulp.

Alkali treated pulp



[MPC]

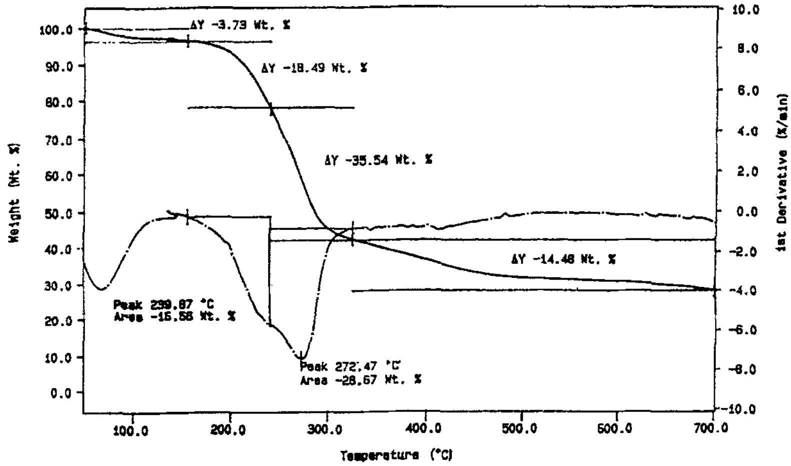
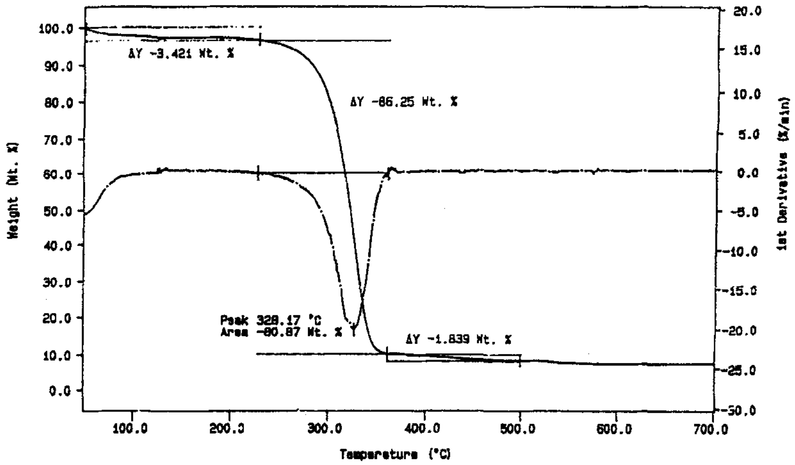


FIGURE 4 TG and DTA thermograms for 5% alkali treated bagasse pulp and the prepared methyl propionate-3-(OCellulose).

penetration of methyl acrylate into lignocellulose fiber was expected. Therefore, the changes in the thermal properties of fiber is observed.

For the case of [PAHC] sample, two main weight loss steps can be seen (Fig. 8), with respective DTG maxima of 279.5°C and 450°C

Alkali treated pulp



[MPC]

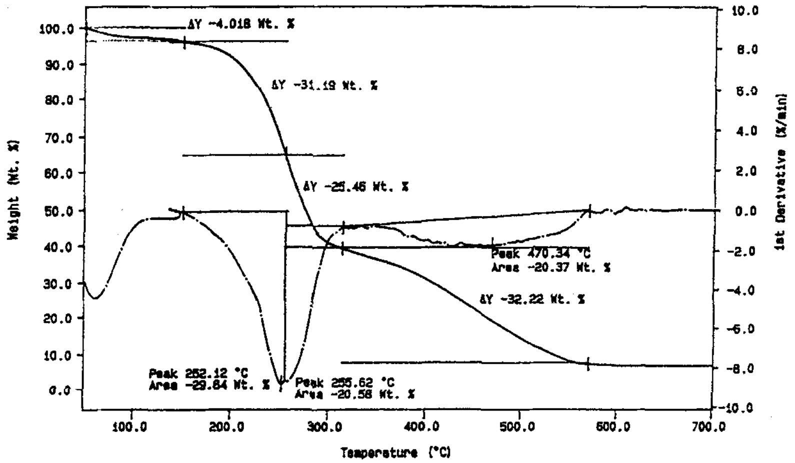


FIGURE 5 TG and DTA thermograms for 10% alkali treated bagasse pulp and the prepared methyl propionate-3-(OCellulose).

corresponding to the active temperature of decomposition. The total activation energy, ΣE_a, required to decomposite [PAHC] is lower than [MPC], this is related to the alkali hydrolysis effect of hydrazine hydrate on cellulose (see C_rD's in Tabs. IV and VIII).

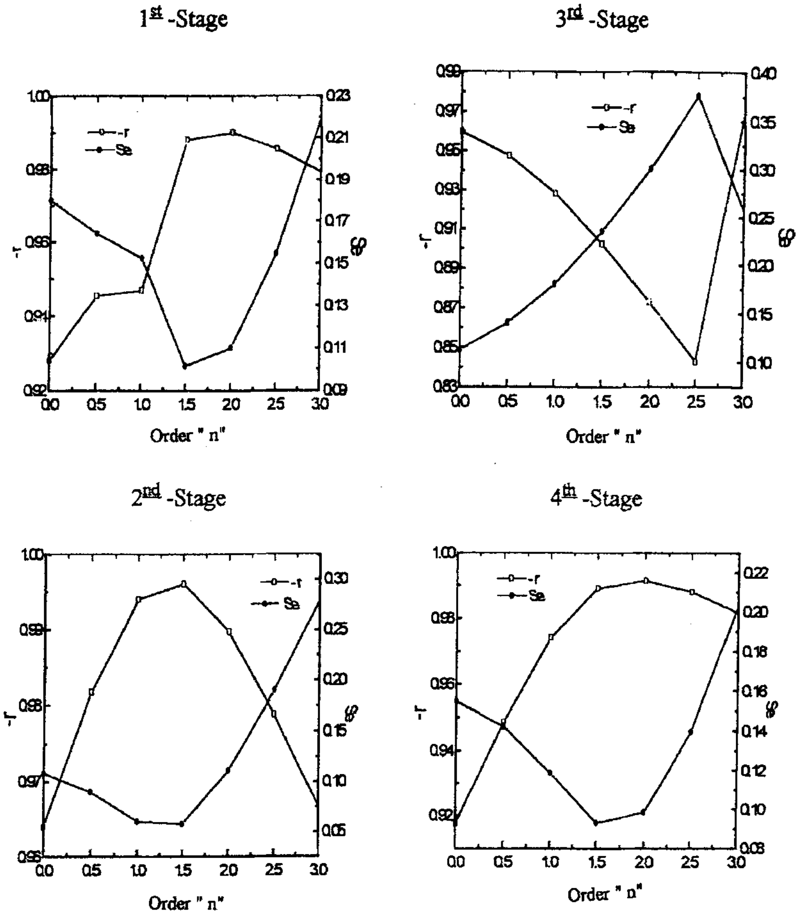


FIGURE 6 Statistical determination of order "*n*" of the main degradation stages of bleached bagasse pulp.

Thermal Analysis of [PAHC]-metal Ions Samples

The TG and DTG of [PAHC]; as adsorbent, treated with some metal salts, *e.g.*, $FeCl_3$, $CrCl_3$, $CuCl_2$, $NiCl_2$, $CdCl_2$, $MnCl_2$ and $MgCl_2$ are illustrated in Figures 8–10. It is clear that, the thermograms of the combined [PAHC] with metal ions (except Cu(II)) have more than two main decomposition stages, in addition to the dehydration stages at temperature ~100°C, which were observed in the case of [PAHC]

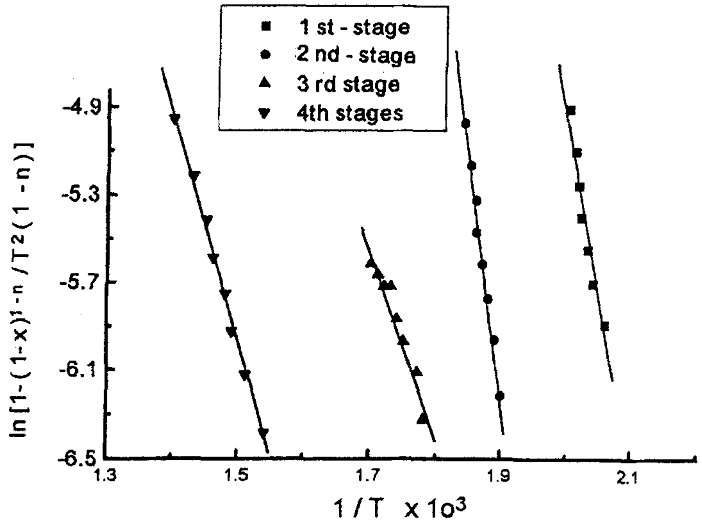


FIGURE 7 Plots of $\ln[1-(1-\alpha)^{1-n}/T^2(1-n)]$ *vs.* $10^3\ T^{-1}$ of the degradation stages of bagasse pulp.

TABLE X Temperature ranges, activation energies, frequency factors and order of the main thermal degradation stages of un-modified and modified bagasse pulps

Sample	*Stage range, K*	*Temp. range, K*	E_a *(kJ/mol)*	*A* *(sec⁻¹)*	*n*
Bleached pulp	1st	482–510	361.64	1.9×10^{34}	1.5
	2nd	519–547	417.6	6.9×10^{36}	1.5
	3rd	550–596	175.7	5.4×10^{11}	0.0
	4th	630–730	194.3	6.9×10^{10}	1.5
			$\Sigma E_a = 1149$		
Alkali Treated Pulp[a]	1st	548–595	254.6	9.5×10^{18}	1.0
	2nd	623–773	121.6	2.3×10^{5}	1.5
			$\Sigma E_a = 376.2$		
Alkali Treated Pulp[b]	1st	555–629	196.4	1.7×10^{3}	1.0
	2nd	629–769	144.3	6.1×10^{6}	1.5
			$\Sigma E_a = 340.7$		
[MPC][a]	1st	463–507	159.30	9.2×10^{12}	0.5
	2nd	509–574	212.80	7.5×10^{16}	2.0
	3rd	595–765	96.98	8.5×10^{2}	1.5
			$\Sigma E_a = 469.0$		
[MPC][b]	1st	462–523	117.94	3.0×10^{8}	0.5
	2nd	526–565	504.91	6.5×10^{44}	2.5
	3rd	629–823	102.86	2.5×10^{3}	1.5
			$\Sigma E_a = 725.7$		
[PAHC]	1st	476–574	94.88	1.5×10^{5}	1.0
	2nd	620–876	80.26	3.6×10^{1}	1.5
			$\Sigma E_a = 175.2$		

(a) 5%NaOH was used either to treated the pulp or to form the alkali cellulose, during Michael addition reaction, and;

(b) 10%NaOH was used either to treated the pulp or to form the alkali cellulose during Michael addition reaction.

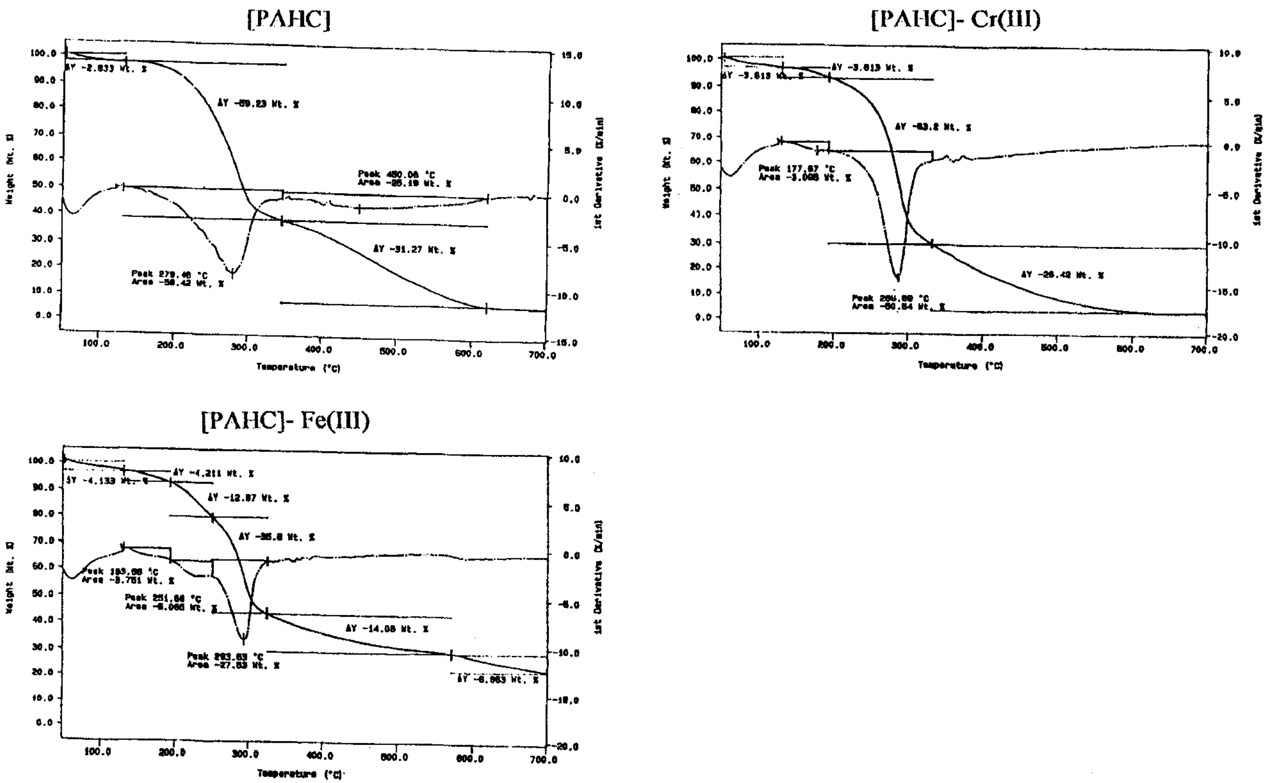
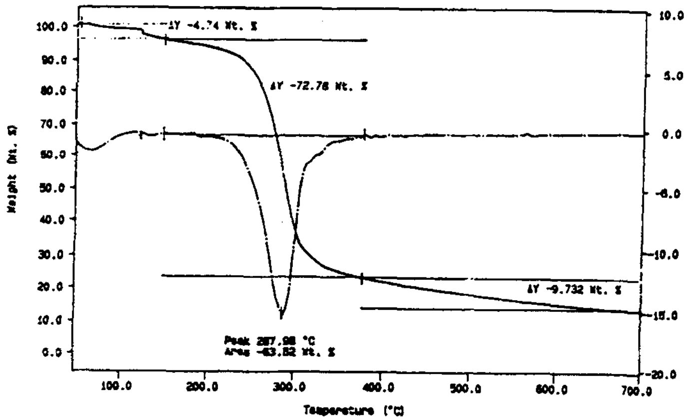


FIGURE 8 TG and DTA thermograms for propionic acid hydrazide-3-(OCellulose) and its combination with Fe(III) and Cr(III) ions.

[PAHC]-Cu(II)



[PAHC]-Ni(II)

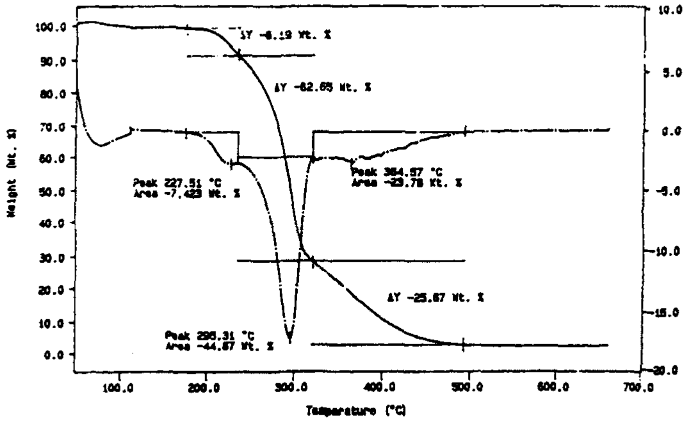


FIGURE 9 TG and DTA thermograms for propionic acid hydrazide-3-(OCellulose) combined with Cu(II) and Ni(II) ions.

thermograms. These additional peaks are due to the release of coordinated water {[PAHC] - Fe(III) and [PAHC]-Cr(III)} or /and the decomposition of metal chelated bonds {[PAHC]-Ni(II), [PAHC]-Mn(II) and [PAHC]-Mg(II)}. While, for the case of [PAHC]-Cu(II) the two decomposition stages with the increase in the initial decomposition temperatures (T_d) are noticed, compared with [PAHC].

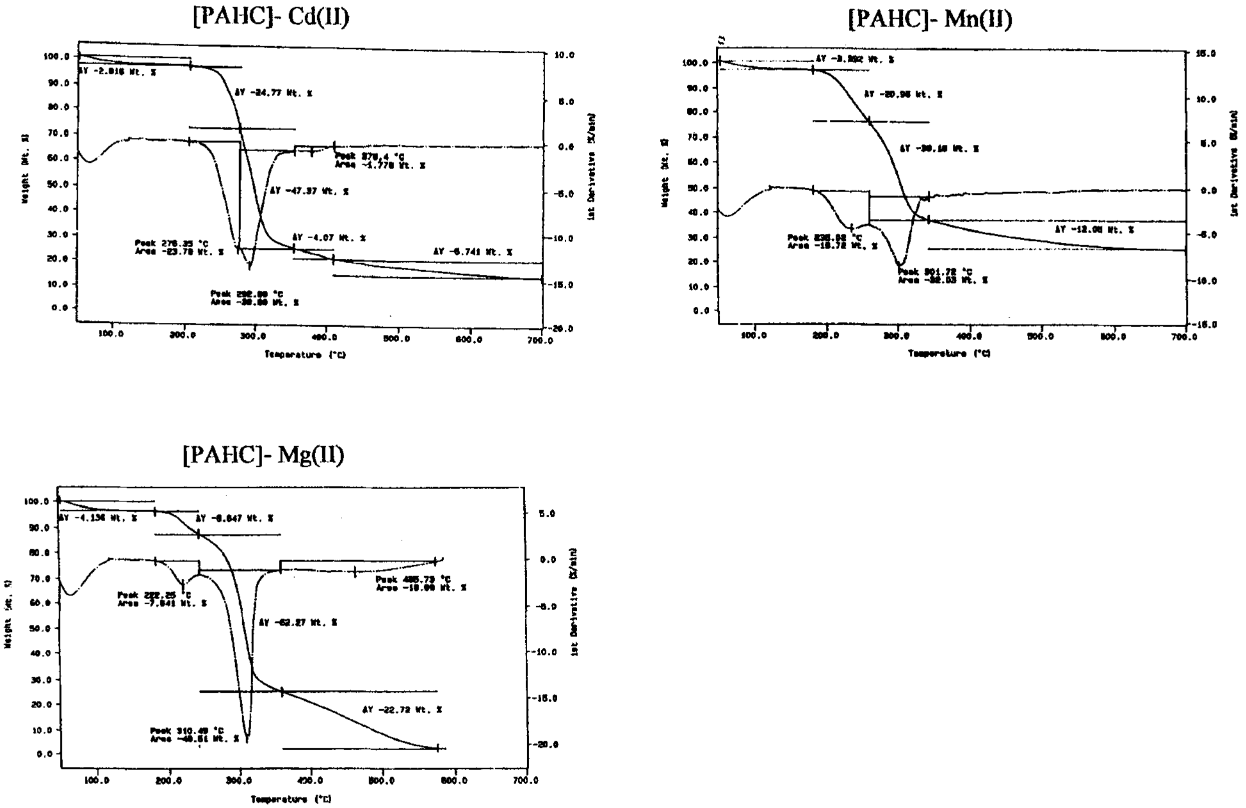


FIGURE 10 TG and DTA thermograms for propionic acid hydrazide-3-(OCellulose) combined with Cd(II), Mg(II) and Mn(II) ions.

Results of Table XI show that, decomposition temperature (T_d) at 10% weight loss for [PAHC] is 210°C; while for [PAHC] combined with metallic ions (except Fe(III)) the decomposition temperatures are shifted to a higher value. The extent of shift behaves the following order : [PAHC]-Cd(II) > [PAHC]-Cu(II) > [PAHC]-Ni(II) > [PAHC]-Mg(II) > [PAHC]-Cr(III) > [PAHC]-Mn(II). The decrease of the decomposition of [PAHC]-Fe(III), compared with [PAHC] this is attributed to the oxidation effect of $FeCl_3$ on the unsubstituted hydroxyl groups of cellulose chains [30, 31]. This view was emphasized from the relatively increased of the relative absorbency, E, corresponding to C=O group and the decreased of, E, corresponding to OH-stretching vibration (Tab. VIII).

A 50% weight loss, the T_d only increased in the case of Mn, Fe(III), Mg(II) and Cd(II) containing [PAHC], whereas the shift in the T_d to the higher temperature in case of [PAHC]- Mg(II) > [PAHC]-Mn(II) > [PAHC]-Fe(III) > [PAHC]-Cd(II), compared with [PAHC]. It can be also seen that, at weight loss, % > 50% no shift in the T_d to higher temperature was observed for most [PAHC]-metal samples.

It may be noted from the above results that, the combination of metallic ions with modified bagasse pulp improves its resistivity to start the decomposition but this is followed by rapid decomposition. The extent of the resistivity depends on the type and amount of metal ion combined with modified bagasse pulp.

The activation energies (E_a) and frequency factors (A), for the various stages of thermal decomposition of [PAHC]-metal ions

TABLE XI Temperature of decomposition, T_d, at different weight losses of [PAHC] and [PAHC]-metal ions samples

Weight loss, %	*Decomposition temps., °C*							
	[PAHC]	*[PAHC]-Fe(III)*	*[PAHC]-Cr(III)*	*[PAHC]-Cu(II)*	*[PAHC]-Ni(II)*	*[PAHC]-Cd(II)*	*[PAHC]-Mg(II)*	*[PAHC]-Mn(II)*
10	219	211	220	237	235	257	232	225
20	246	248	257	260	262	271	279	249
30	266	276	271	271	271	280	295	277
40	280	290	281	280	284	289	303	293
50	293	301	291	286	292	297	308	307
60	330	351	299	294	300	305	315	321
70	430	554	334	311	312	323	326	447

TABLE XII Temperature ranges, activation energies, frequency factors and order of the main thermal degradation stages of [PAHC] and [PAHC]-metal ions samples

Sample	*Stage*	*Temp. range, K*	E_a *(kJ/mol)*	*A* (sec^{-1})	*n*	*Coordinated* H_2O*, %*
[PAHC]	1st	476–574	94.88	1.5×10^5	1.0	–
	2nd	620–875	80.26	3.6×10^1	1.5	
			$\Sigma E_a = 175.2$			
[PAHC]-Fe(III)	1st	465–517	183.74	4.5×10^{15}	1.5	4.211
	2nd	526–585	248.04	2.1×10^{19}	1.5	
	3rd	615–826	99.07	6.1×10^4	2.0	
	4th	856–973	303.09	1.6×10^{13}	2.0	
			$\Sigma E_a = 833.9$			
[PAHC]-Cr(III)	1st	500–593	131.86	4.9×10^8	1.0	3.613
	2nd	624–873	130.40	1.3×10^6	3.0	
			$\Sigma E_a = 262.3$			
[PAHC]-Cu(II)	1st	493–616	149.03	1.6×10^{10}	1.5	–
	2nd	659–930	161.88	3.6×10^7	3.0	
			$\Sigma E_a = 310.9$			
[PAHC]-Ni(II)	1st	473–500	372.40	1.3×10^{36}	1.5	–
	2nd	514–584	161.28	1.5×10^{11}	1.0	
	3rd	614–754	202.33	1.3×10^{12}	2.5	
			$\Sigma E_a = 736.0$			
[PAHC]-Cd(II)	1st	505–549	324.90	1.5×10^{11}	1.5	–
	2nd	552–607	209.10	1.3×10^{17}	2.0	
	3rd	628–684	111.97	1.1×10^4	1.0	
			$\Sigma E_a = 706.0$			

[PAHC]-Mg(II)	1st	478 – 518	302.50	1.5×10^{13}	2.0	8.65
	2nd	526 – 605	158.25	2.1×10^{10}	0.5	
	3rd	634 – 836	81.26	4.7×10^{1}	1.0	
			$\Sigma E_a = 542.0$			
[PAHC]-Mn(II)	1st	473 – 533	168.79	3.1×10^{13}	1.0	–
	2nd	541 – 600	218.46	1.1×10^{16}	1.5	
	3rd	619 – 835	99.91	6.3×10^{4}	2.0	
			$\Sigma E_a = 487.2$			

samples, which were determined from the slopes and intercepts, respectively, of the plots of $\log_{10}[1-(1-\alpha)^{1-n}/T^2(1-n)]$ *vs.* $1/T$ are registered in Table XII. It is clear that the total activation energies, ΣE_a, of the decomposition stages in the case of [PAHC]-metal ions samples are higher than [PAHC]. These values behave the following sequence: [PAHC]-Fe(III) > [PAHC]-Ni(II) > [PAHC]-Cd(II) > [PAHC]-Mg(II) > [PAHC]-Mn(II) > [PAHC]-Cu(II) > [PAHC]-Cr(III). This sequence is probable related to the electronegativity of metal ions, strength of the bond between the adsorbent and metal ion, and the amount of metal ion included the cellulose derivative (Tab. IX).

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