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CHARACTERIZATION OF MODIFIED OXYCELLULOSE

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Abstract

Sodium, ferric and aluminum salts of oxycellulose and the amphoteric ion exchanger derivatives from cationized oxycellulose were prepared. Thermal behaviour of the different samples was investigated by thermal gravimetric analysis (TG) and derivative thermogravimetric (DTG) technique. The rate constant and the activation energy were estimated. Infrared spectroscopy of the different samples were investigated, analyzed and discussed.

Keywords: activation energy, cellulose derivative, DTG, IR, oxycellulose, rate constant, TG

Introduction

Cellulose ion exchangers are of increasing interest and find various industrial applications [1]. Cation and anion exchangers could be prepared from cellulose by introduction of substituent groups with basic or acidic properties. Solubility or swellability of the products in weak acid or weak base medium should be avoided by preparing a product of lower degree of substitution or by crosslinking. Amphoteric cation exchange derivatives could be prepared, as described earlier [2], by reacting the anionic oxycellulose with different ratios of cationizing agent containing diepoxypropyl dimethyl ammonium chloride. This agent contains a quaternary ammonium group for cationization, and diepoxy groups for crosslinking at the same time.

The modification of oxycellulose by cationization or by salt formation allows to obtain a new material with different structural characteristics, which can be reflected in their thermal decomposition process. The thermal analysis techniques as thermal gravimetric analysis (TG) and derivative thermogravimetry (DTG) provide a powerful tool to study the behaviour of such cellulosic materials during their thermal degradation. The kinetic of the mass loss is used to elucidate the rate constant of decomposition and the activation energy. IR spectroscopy using the potassium bromide disk technique has been shown to be a useful tool to investigate the fine structure charac-

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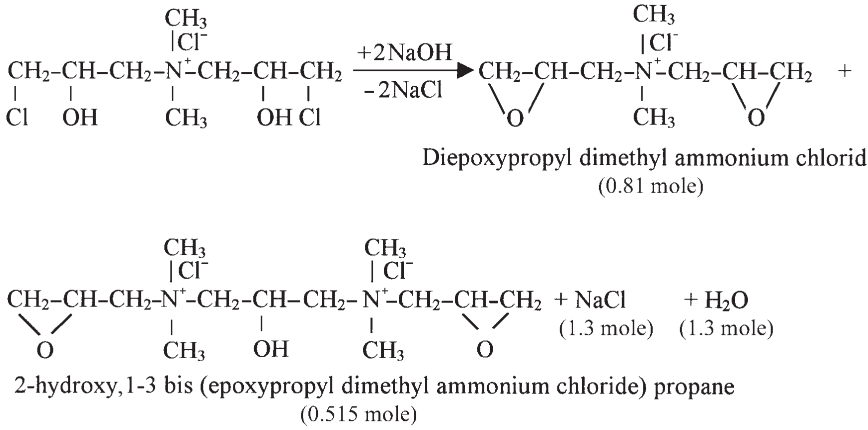
teristics of cellulose and chemically modified cellulose. A slight difference in IR spectra may signal differences in the ratio of constituent units and the order in which they are linked [3]. In the present investigation, results of TG, DTG and IR spectra of modified oxycellulose have been analyzed and discussed.

Experimental

Monocarboxy cellulose (MCC) prepared by N_2O_4 oxidation, which has carboxyl content 17.2, carbonyl group 1 and ash 1.23%, was obtained from Synthesia A. S., Pardubice-Semtin, Czech Republic.

Refaktan K, from Chemotex, A.S., Decin 32 – Boltice nad Labem, Czech Republic, was activated before using by mixing 1 kg of Refaktan K with 1.33 mole NaOH with gentle stirring to full solubility of both compounds. After activation Refaktan K has the given structure.



Other chemicals are of the analytical grade and used without further purification.

Analyses

TG were recorded by Perkin Elmer, Thermal Analysis Controller, TAC 7/DX TGA7.

IR were recorded by JASCO FT/IR – 300E Fourier Transform Infrared Spectrometer by using the potassium bromide disk technique in the range 4000–200 cm^{-1}.

Carboxyl content, nitrogen content and ionactivity measurement were estimated as described earlier [2]. Na, Al(III) and Fe(III) were estimated by atomic absorption analyses

Monocarboxy cellulose salts

Sodium salt used in this study is prepared by reacting 1 M monocarboxy cellulose (176 g) with 2 M NaOH in aqueous medium with liquor ratio 5:1 (5 cm^3 H_2O :1 g MCC) for one h at room temperature. After the reaction time, acetic acid was used for neutralization and ethyl alcohol used for precipitation. The 89.5% yield of white fine powder with 1.61% of residual carboxyl group was obtained.

Fe(III) and Al(III) salts were prepared by treating 1 M of monocarboxy cellulose sodium salt with 0.33 M of Fe(III) or Al(III) as ($FeCl_3$ or $AlCl_3$) with stirring at room temperature for one h in aqueous medium at liquor ratio 5:1, using ethyl alcohol for precipitation and washing. The obtained yield were 108 and 106% with residual carboxyl group 2.69 and 0.31% for Fe(III) and Al(III) respectively.

Cationized monocarboxy cellulose

Monocarboxy cellulose was treated with the cationizing agent in aqueous medium at liquor ratio 10:1 and pH adjusted to 9 by 25 % NaOH solution with occasional shaking at 70°C for 60 min. After the reaction time 0.2 M H_2SO_4 was used for neutralization to pH 6.8. The reaction solution was cooled to room temperature, acetone (30 cm^3 g^{-1}) was added to precipitate the product, followed by filtration through G_2 sintered glass funnel, washing with acetone and air-drying. The cationizing agent percent varied from 0 to 100% (relative to monocarboxy cellulose) to obtain products of different nitrogen content.

Results and discussion

The cationizing agent percent to monocarboxy cellulose in the reaction medium was varied from 0 to 100% to obtain different degrees of cationized oxycellulose. As the cationizing agent percent increased the cation activity of the product increased and the anion activity decreased. Table 1 summarizes the properties of the different samples used in this study.

Table 1 Ion exchange properties and the degree of substitutions (DS) of the investigated samples

Sample	Cationizing agent/%	Yield/%	N/%	Metal/%	DS	Exchange capacity/ mmol g^{-1}	
						As cation	As anion
Oxycellulose	0	100.0	0.00	–	0.00	0.00	1.80
2	2	105.8	0.23	–	0.03	0.09	1.74
4	10	107.8	0.74	–	0.10	0.34	1.54
5	20	115.7	1.24	–	0.15	0.87	1.01
7	100	147.5	2.27	–	0.35	2.15	0.00
Na salt	–	89.5	–	8.22	0.79	–	–
Al salt	–	106.0	–	4.90	1.00	–	–
Fe salt	–	108.0	–	8.32	0.85	–	–

Thermal properties

The thermal behaviour of the different samples was investigated by thermogravimetric analysis (TG). The analysis was carried out from room temperature to 900°C under nitrogen atmosphere and at a heating rate of 10°C min^{-1}. Samples were also analyzed by derivative thermogravimetry (DTG) to aid in the identification of the decomposition behaviour of the investigated samples.

Table 2 Temperatures of decomposition at certain mass losses %

Sample	Temperatures of decomposition (°C) at mass losses % of							
	10	20	30	40	50	60	70	80
MCC[*] (a)	148	180	208	250	285	312	355	398
2 (b)	120	173	185	212	248	350	660	700
4 (c)	153	175	190	220	250	350	675	780
5 (d)	158	177	197	232	273	405	655	770
7 (e)	157	177	198	215	245	290	450	700
Na salt (f)	148	172	200	223	275	450	685	–
Al salt (g)	125	198	237	269	285	330	365	430
Fe salt (h)	160	195	235	245	278	352	428	500

[*] MCC is the monocarboxy cellulose raw material

Figure 1 shows the TG and DTG curves for the different samples. It could be seen in the figure and in Table 2 that after the moisture content loss and evaporation of the volatile materials at about 150°C the mass of all samples decreases sharply. The main decomposition of the samples amounting to about 50% of the total mass is observed over the temperature range 245–285°C. Oxycellulose raw material shows a complete sharp decomposition to constant mass at 450°C. DTG curve of oxycellulose (Fig. 1a) shows three maximum decomposition peaks at 200, 300 and 425°C. These peaks of degradation could be referred to the early dehydration, fragmentation and finally degradation of the carbohydrate residues respectively. The thermal stability of oxycellulose after 50% mass loss, at temperature >300°C was improved by cationization or by salt formation.

The cationized samples (Fig. 1, b–e) show a steep mass loss over the temperature range 300–650°C amounted to about 11–16% of the total mass, followed by a gradually mass decrease until a constant mass obtained at 700, 800, 900 and 900°C for samples 2, 4, 5 and 7, respectively. DTG curves for the cationized samples shows two maximum main decomposition peaks, the first at 225, 212, 200 and 200°C, while the second peaks at 700, 750, 750 and 775°C for the samples 2, 4, 5 and 7, respectively. The second decomposition peak temperature, which was not found in the oxycellulose, could be related to the introduced cationic group. This means that the thermal stability of the cationized products, at higher temperature, depends on their degree of substitution (nitrogen content) on a direct relationship.

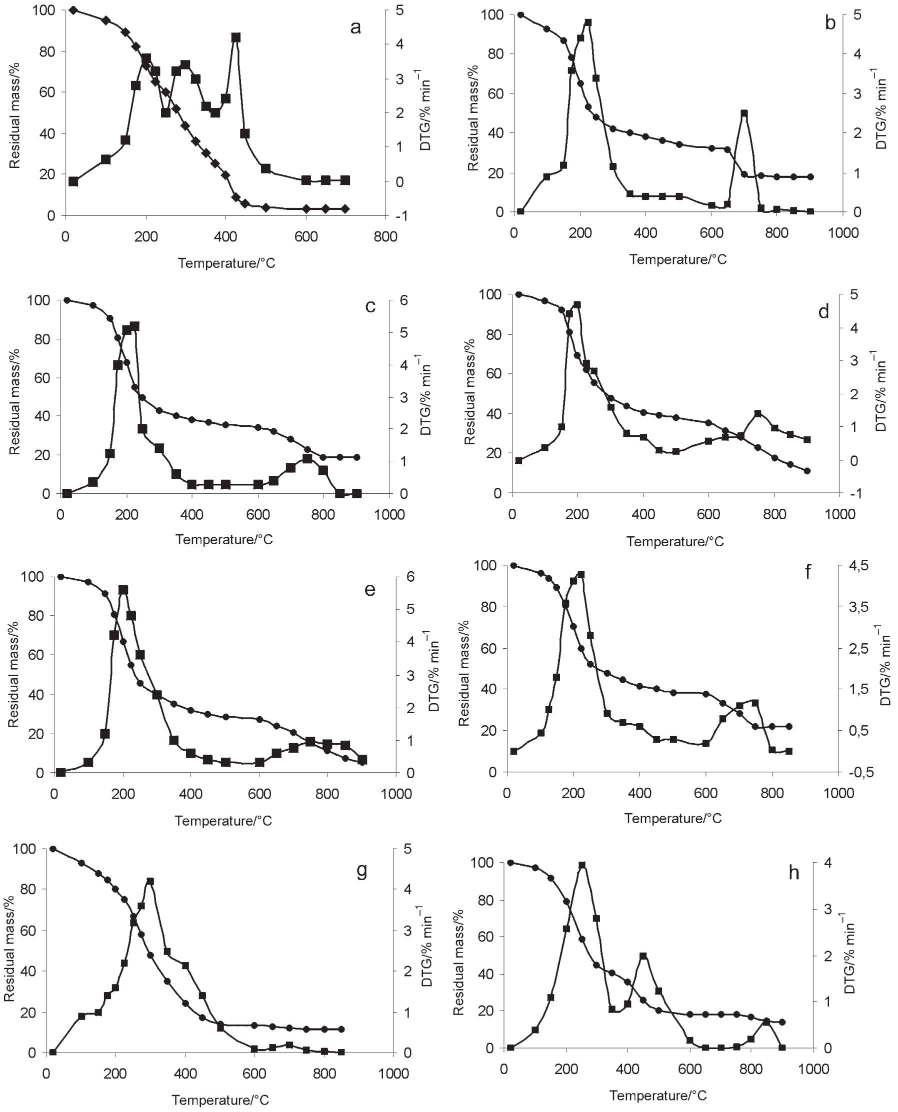


Fig. 1 TG and DTG curves for different samples. Sample numbers are the same as in Table 2

During thermal decomposition measurements oxycellulose salts behave nearly in the same way as oxycellulose itself until mass loss reaches 50%, after that Al(III) salt shows a little stability until a nearly constant mass at 500°C. Fe(III) salt shows a little higher stability than Al(III) salt until a nearly constant mass at 500°C. Than it losses 3% of its mass by raising the temperature from 500 to 800°C and loses further 3% by increasing the temperature from 800 to 850°C, then the mass becomes constant. After 50% mass loss at 275°C Na salt shows a steep loss of 13% over the tem-

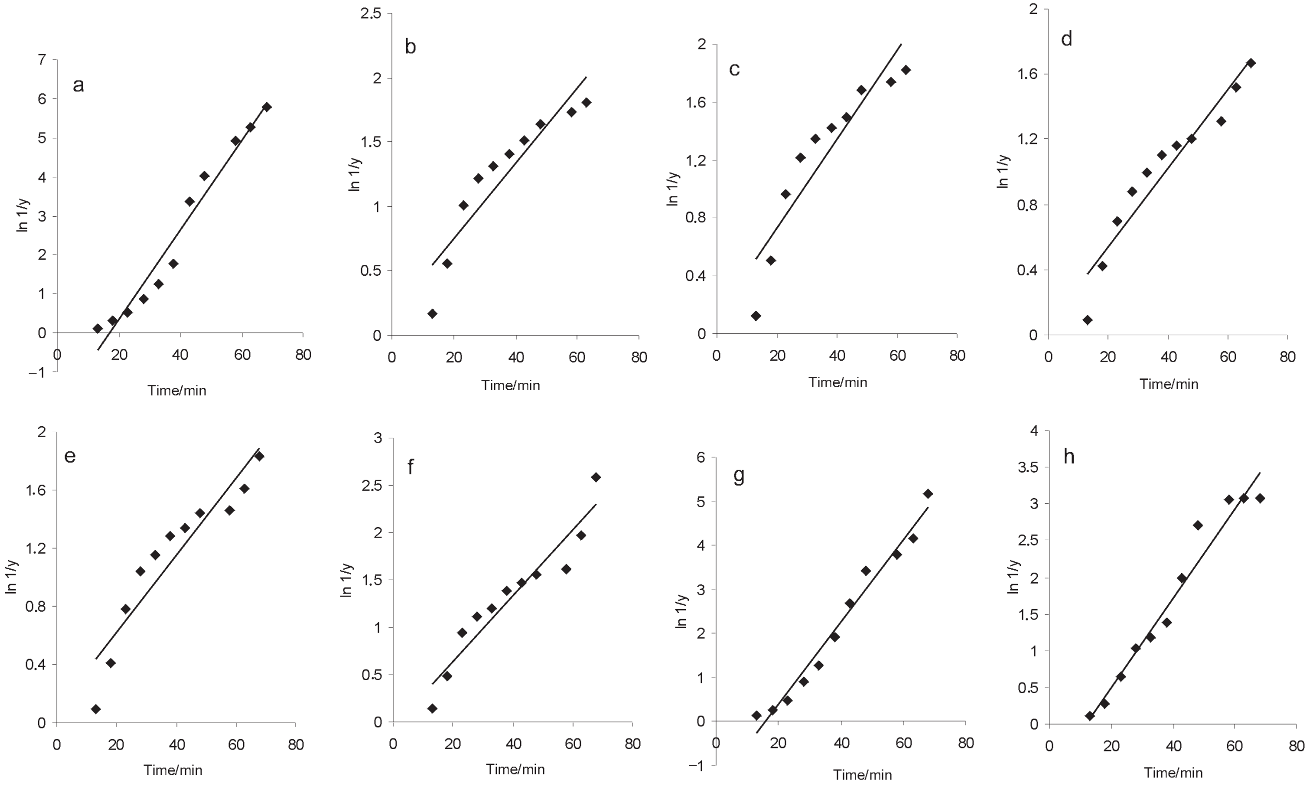


Fig. 2 ln 1/*y* *vs*. time

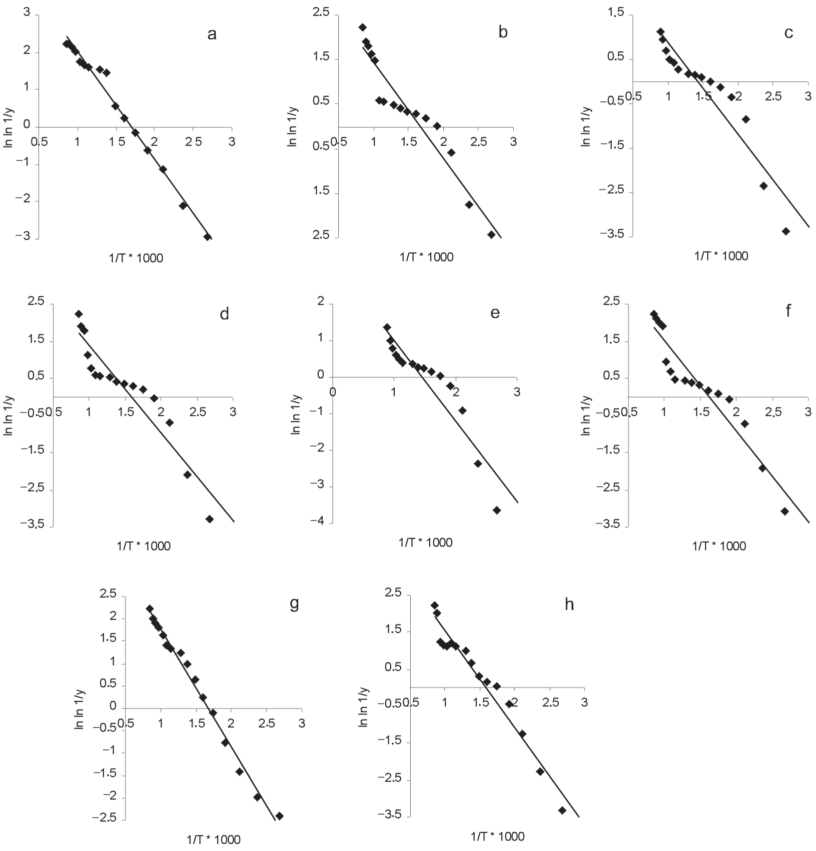


Fig. 3 ln(ln1/y) *vs.* 1/T

perature range 275–600°C, and a gradual mass loss of 15% over the temperature range 600–750°C. DTG curves of oxycellulose salts (Fig. 1, f–h) show only one wide decomposition peak for Al(III) salt with a maximum at 300°C, while for Fe(III) salt there are three maximum decomposition peaks at 250, 450 and 850°C. For Na salt two mean decomposition peaks at 225 and 725°C were observed. In conclusion, Al(III) and Fe (III) salts slightly improve the thermal stability of the oxycellulose, while Na salt shows the maximum thermal stability among other salts and also among the cationized samples.

Calculation of the rate constant

The rate constant (k) could be calculated from the relation between the mass fraction and the time [4], where

$$-\ln 1/y = kt + constant \qquad (1)$$

y is the mass fraction not yet decomposed at time t,

$$y=(W_t-W_\infty)/(W_0-W_\infty) \tag{2}$$

where, W_t is the mass at time t, W_∞ is the mass at the end of the reaction and W_0 is the original mass of the sample.

The rate constant k was calculated from the slope of the plot of $\ln 1/y$ *vs.* the time [5]. The produced straight line indicating that the degradation of the different samples follows the first order reaction. Figure 2 shows the plots of $\ln 1/y$ *vs.* the time for the different investigated samples. The rate constant k was calculated and the obtained results are displayed in Table 3.

Table 3 Rate constant and activation energy for different samples

Sample	R. M.	2	4	5	7	Na salt	Al salt	Fe salt
Rate constant/ min^{-1}	0.942	0.238	0.256	0.204	0.200	0.286	0.782	0.511
Activation energy/J mol^{-1}	19950	14660	14660	16630	18330	17240	18180	18180

From the results it could be noticed that the rate constant values is higher for the samples of lower thermal stability. Oxycellulose raw material (MCC) has the highest values followed by the Al(III) salt. On proceeding of the cationization reaction (samples 2, 4, 5 and 7) the rate constant decreased gradually, its values are about one fourth of that for raw material. The formation of salts also decreases the rate constant in the order Na>Fe>Al.

Calculation of the activation energy

Activation energy was calculated from TG data according to Broido method [4]. He stated that

$$\ln(\ln 1/y)= -E/RT+constant$$

where y is the mass fraction (Eq. (2)) and T is the absolute temperature.

Thus, a plot of $\ln(\ln 1/y)$ *vs.* $\ln 1/T$ yields a straight line whose slope is equal to E/R. Figure 3 shows the plot between $\ln(\ln 1/y)$ and $\ln 1/T$. Table 3 presents the values of the activation energy for the different samples investigated. It is obvious that oxycellulose has the higher value of activation energy followed by Fe(III) and Al(III) salts. The cationized samples show higher activation energy for the higher substituted samples.

Infrared spectra

The relative absorbance of different bands (RA) was determined following the base line correction method for making a comparative study of the spectra [6]. The 1160 cm^{-1} band, assigned to asymmetric vibration of C–O–C in cellulose molecules, has been chosen as an internal standard, to determine the relative absorbance. IR data are also analyzed by the base line optical density method [7] to confirm the results.

The summary of band positions and the corresponding relative intensities (to the band at 1160 cm^{-1}) and the relative optical density are given in Table 4.

Table 4 Infrared spectra, relative intensity and relative optical density

Band position	MCC		2		4		5		7	
	R A	OD	R A	OD	R A	OD	R A	OD	R A	OD
3440	6.55	0.62	7.60	0.70	8.31	0.74	12.7	0.79	14.2	0.85
2900	2.28	0.09	2.60	0.13	2.88	0.15	3.31	0.18	3.36	0.23
1610	10.90	1.33	10.2	0.91	10.1	0.86	9.19	0.68	8.42	0.50
1416	5.69	0.65	5.30	0.53	4.91	0.46	4.56	0.44	4.36	0.40
1340	0.38	0.30	0.39	0.27	0.42	0.21	0.44	0.18	0.48	0.10
1310	1.85	0.11	1.92	0.17	2.01	0.19	2.22	0.21	2.34	0.25
1240	0.44	0.24	0.50	0.30	0.55	0.30	0.59	0.35	0.61	0.37
1060	5.72	0.72	5.82	0.78	6.09	0.81	7.78	0.87	8.10	0.95
950	0.15	0.10	0.30	0.15	0.36	0.20	0.78	0.35	1.00	0.50
900	2.20	0.46	2.31	0.43	2.31	0.35	2.44	0.25	2.60	0.22
600	2.40	0.23	2.91	0.34	3.46	0.38	5.11	0.42	6.00	0.43

Sample numbers are the same as in Table 2

The band at 3440 cm^{-1} is attributed to hydrogen bonded O–H stretching vibration, its relative absorbance intensity increased by cationization due to the presence of OH groups in the introduced cationic group. The C–H stretching vibration absorbance intensity ratio at 2900 cm^{-1} increased with increasing the substitution degree due to the presence of CH_2 groups in the introduced group. The absorption bands at 1610 cm^{-1}, attributed to the vibration of adsorbed water molecules as well as to the carboxylate anion COO^-, has lower absorbance intensity ratio for higher substituted samples due to the blocking of the carboxyl group by the reaction. The band at 1416 cm^{-1} is attributed to COO^- ion and/or to O–H bending in COOH, it also assigned to the crystalline cellulose form. This band has a lower absorbance intensity ratio for substituted samples as compared with the oxycellulose. The band near 1340 cm^{-1} in the IR spectra, attributed to both C–N vibrations as well as to O–H in-plane deformation [8], has higher absorbance intensity ratio for higher substituted samples because the introduced quaternary group contains both C–N and O–H groups. The 1310 cm^{-1} band assigned to CH_2 wagging and to O–H bending has higher absorbance intensity ratio for higher substituted samples for the above reason. The band at 1240 cm^{-1} attributed to ring symmetric stretching in epoxide and to O–H in-plane bending and also to C–O stretching has higher absorbance intensity ratio for higher substituted samples because the introduced quaternary group contains an epoxide group as well as C–O and O–H bonds. The band at 1060 cm^{-1} is attributed to skeletal vibrations involving stretching of C–O and C–C bonds attached to the glucose rings. The band at 950 cm^{-1} is attributed to the asymmetric $N–C_4$ stretching [8] shows an increase in the absorbance intensity ratio with the increase of the substitution degree due to the presence of the $N–C_4$ group in the cationizing agent. The band at 900 cm^{-1} is attributed to the asymmetric out-of-plane ring stretching in cellulose due to β-linkage [9] and also attributed to the amorphous form in cellulose, the absorbance intensity ratio decreased with the increase of the substitution degree. The O–H out-of-plane bending vibration at 600 cm^{-1} has higher absorbance intensity ratio for higher substituted samples.

Conclusions

TG and DTG curves of oxycellulose and its derivatives show a sharp decrease in the sample mass to about 50% of its total mass at the temperature range between 150 to 245–285°C. Oxycellulose decomposed to a constant mass at 450°C while the thermal stability of the cationized products improved, at higher temperature, and depends on their degree of substitution (nitrogen content) on a direct relationship. Al(III) and Fe(III) salts slightly improve the thermal stability of the oxycellulose, while Na salt shows the maximum thermal stability among other salts and also among the cationized samples. The rate constant values are higher for the samples of lower thermal stability. Oxycellulose has the higher values of activation energy followed by Fe(III) and Al(III) salts. The cationized samples show higher activation energy for the higher substituted samples.

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