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Thermal behaviour of some homogeneously esterified products of high α-cellulose pulps of fast growing plant species

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Abstract

High α-cellulose pulps obtained from fast growing plant species *Leucaena leucocephala* and *Hibiscus cannabinus* were esterified with trimellitic anhydride (TMA), phthalic anhydride (PTA) and trimethyl acetic anhydride (TMAA), following a homogeneous reaction procedure. The degree of substitution achieved was found to vary, up to 2.56, depending on the reaction conditions. Thermal decomposition was studied by a differential thermogravimetry at three heating rates 5, 10 and 20°C min^{-1} in static air. The kinetic parameters were evaluated using the generalized equation of Coats and Redfern. The thermal stabilities of the esters were found to vary in the order TMA > PTA > TMAA. The decomposition process was found to conform to first order weight loss kinetics, and the activation energies of the respective esters at 5°C min^{-1} heating rate were 308.11, 194.98 and 213.00 kJ mol^{-1} respectively.

INTRODUCTION

In view of the tremendous increase in the consumption of forest based cellulosic materials for pulp and paper making, a global shortage of conventional raw materials by the end of this century can be visualized [1]. The search for new fibre crops has been underway during the last three decades or so, to find and develop new fibre supplies for paper and cellulose industries. The fast growing plant fibres have gained considerable importance as an economic source of cellulosic material and during recent years, many such fast growing annual and perennial plant species have been identified, cultivated and studied for their suitability as alternative sources of raw material for the pulp and paper industry [2–5]. A few studies have also been performed relating to the preparation of high α-cellulose pulp

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and cellulose derivatives from fast growing plant biomass [6–8]. The two fast growing plant species *Leucaena leucocephala* (a perennial plant) and *Hibiscus cannabinus* (an annual plant) have been exploited to prepare high α-cellulose pulp with characteristic physico-chemical properties [9, 10]. Cellulose esterified products have also been prepared by adopting homogeneous esterification procedure [11]. Acetylated products from the α-cellulose obtained from *Leucaena leucocephala* have been prepared and the products have been characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques [12]. The thermal decomposition of the α-cellulose and the acetylated products have also been studied using thermogravimetric and differential thermal analyses, in order to obtain insight into the mechanisms of thermal degradation [13]. Further, homogeneous esterification of α-cellulose pulp (prepared from both the plants as raw materials) has been carried out with trimethyl acetic anhydride (TMAA) and trimellitic anhydride (TMA) under different reaction conditions; the esterified products have been isolated and characterized [14]. Homogeneous esterification of the α-cellulose pulp has also been attempted with a dicarboxylic acid anhydride, e.g. phthalic anhydride (PTA), and the results reported [15]. The esters from TMAA exhibit elastomeric and thermoplastic properties and can be used for the preparation of films and membranes. TMA esters can also be cast from solution and used for water-insoluble coatings. The PTA esters are known for their use as enteric coatings and enteric film coatings of medicinal tablets [16].

In the present communication, we report the thermal behavior and primary physico-chemical characteristics of cellulose-esterified products of TMA, PTA and TMAA, because the thermogravimetric studies of these esters prepared under homogeneous esterification conditions have not yet been reported in the literature.

EXPERIMENTAL

Preparation of esterified products

α-Cellulose pulps extracted from *Leucaena leucocephala* and *Hibiscus cannabinus* contain 94.04 and 94.40% α-cellulose respectively [9, 10]. For preparing TMA and TMAA esters, the α-cellulose pulp from *Leucaena leucocephala,* and for PTA esters the α-cellulose pulp from *Hibiscus cannabinus* were used. The celluloses were dissolved separately in a paraformaldehyde (PF) and dimethyl sulfoxide (DMSO) mixture. The PTA and TMA were dissolved in pyridine by mild heating and homogenoeus esterification was carried out at 80–100°C for 8 h; the esterification with TMAA was carried out at room temperature (27°C) for 1 h.

Thermal analysis

Differential thermal analysis (DTA), thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out using a Shimadzu model 30 thermal analyser model. The weight of the samples for TMA and TMAA esters were in the range 10.0–16.6 mg and 8.0–14.2 mg respectively; for the PTA ester, the range was 10.0–18.7 mg. α-Alumina was used as reference material and the temperature ranged from 25 to 600°C at heating rates 5, 10 and 20°C min^{-1} in static air.

RESULTS AND DISCUSSION

Analysis and characterization of esterified products

The physical characteristics and average degree of substitution (DS) of TMAA and TMA esters were recorded. The degree of sutstitution of the 1 h esterified products of TMAA and the 8 h esterified product of TMA were 2.56 and 2.41 respectively [17]. The phthaloyl content of the dicarboxylic acid ester was 53.6% [18].

The TMAA and TMA esters were characterized by IR and ^{1}H NMR spectroscopies. The IR spectra of the 1 h esterified product of TMAA showed characteristic ester bands at 1740 cm^{-1}. The TMA esters also exhibited bands characteristic of the ester compounds at 1740 (C=O), 1260 and 1300 cm^{-1} (–C–O–C–, asymmetric stretch) and 1080 cm^{-1} (–C–O–C–, asymmetric stretch), which are characteristic of aromatic esters having the C_6H_5–C(=O)–C–R formula [19]. The IR spectra of PTA esters also showed the sharp absorption bands at 1740 cm^{-1} characteristic of the carbonyl group [15].

In the ^{1}H NMR spectra of TMAA, the resonance observed at 1.15 and 4.85 δ are indicative of the formation of esterified cellulose products. The ^{1}H NMR spectra of TMA esters with absorption peaks at 7.90, 8.20 and 8.45 δ is indicative of the presence of the three aromatic protons of the trimellitic group attributed to H-5′, H-6′ and H-3′ respectively. The resonance signals due to H-6 (–CH_2–O–) and H-4 appeared between 4.0 and 6.2 δ. The details of this study have been reported elsewhere [14].

Thermogravimetric analysis

The thermal analyses (TG, DTG and DTA) of the three esters studied are shown in Figs. 1, 2 and 3 at heating rates of 5, 10 and 20°C min^{-1} for each. The thermal analysis data are summarized in Tables 1A–1C. Thermograms are shown separately in Figs. 4(a) and 4(b) for heating rates of 5 and 10°C min^{-1}; from these it is clear that the esters may be grouped according to decreasing thermal stability in the order TMA > PTA > TMAA. However, there appears to be a transition below which the thermal stability of the

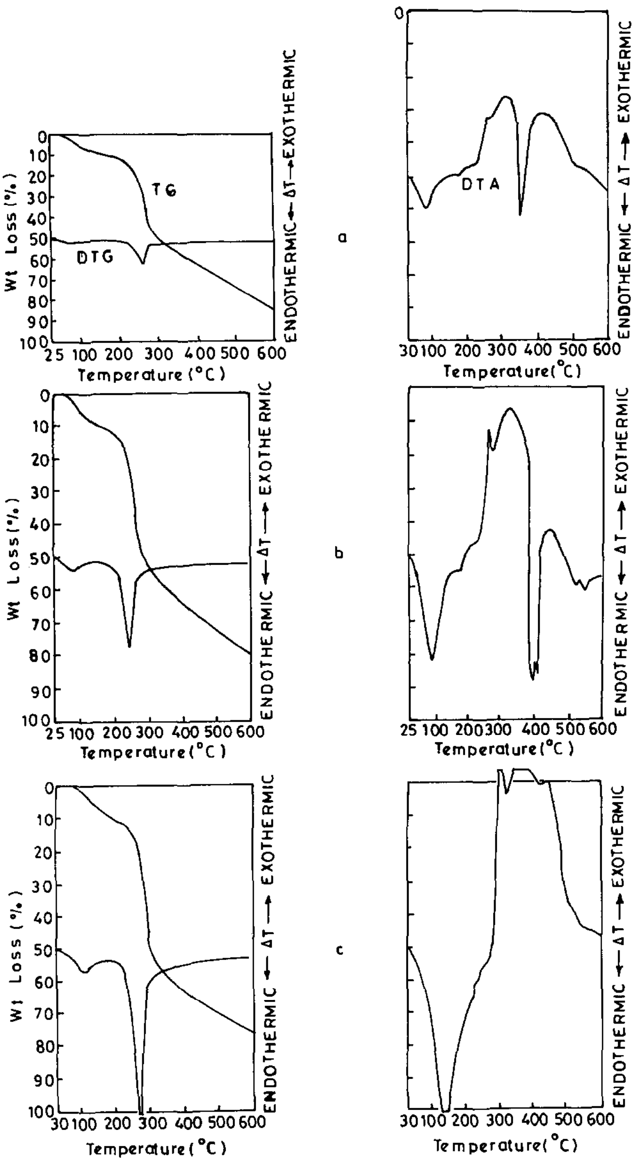

Fig. 1. TG, DTG and DTA analyses of the TMA cellulose esters at heating rates of (a) 5, (b) 10 and (c) 20°C min^{-1}.

TMAA ester is increased, as can be inferred from the relative lowering in rate of weight loss below this temperature.

DTA curves for the TMA ester at heating rates 5 and 10° min^{-1} are almost identical. An endothermic process starts at 25–30°C and extends up to 140–160°C. This is due to the loss of moisture by slow evaporation. Following this there is an exothermic process with a maximum at 316°C, which is higher than the TG decomposition temperature. The exothermic

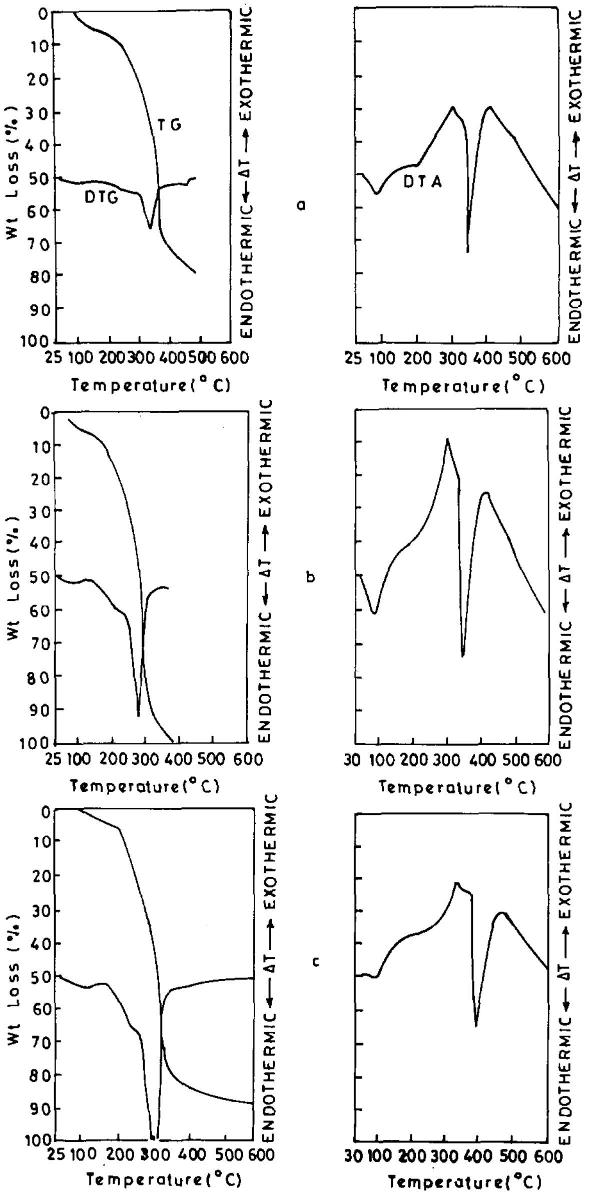

Fig. 2. TG, DTG and DTA analyses of PTA esters at heating rates of (a) 5, (b) 10 and (c) 20°C min^{-1}.

peak is wide and extends up to 600°C, with small intermediate peaks, built onto the overall process. This may be attributed to rapid decomposition reactions occurring parallel to the main decomposition process and may be due to the prevalence of an oxidative environment. Referring to the DTA curves obtained for α-celluloses [20], the new large endothermic peak in the DTA curve for the TMA ester (Fig. 1), may be reasonably assigned to the breakdown of the ester group; subsequent peaks at 430–445°C

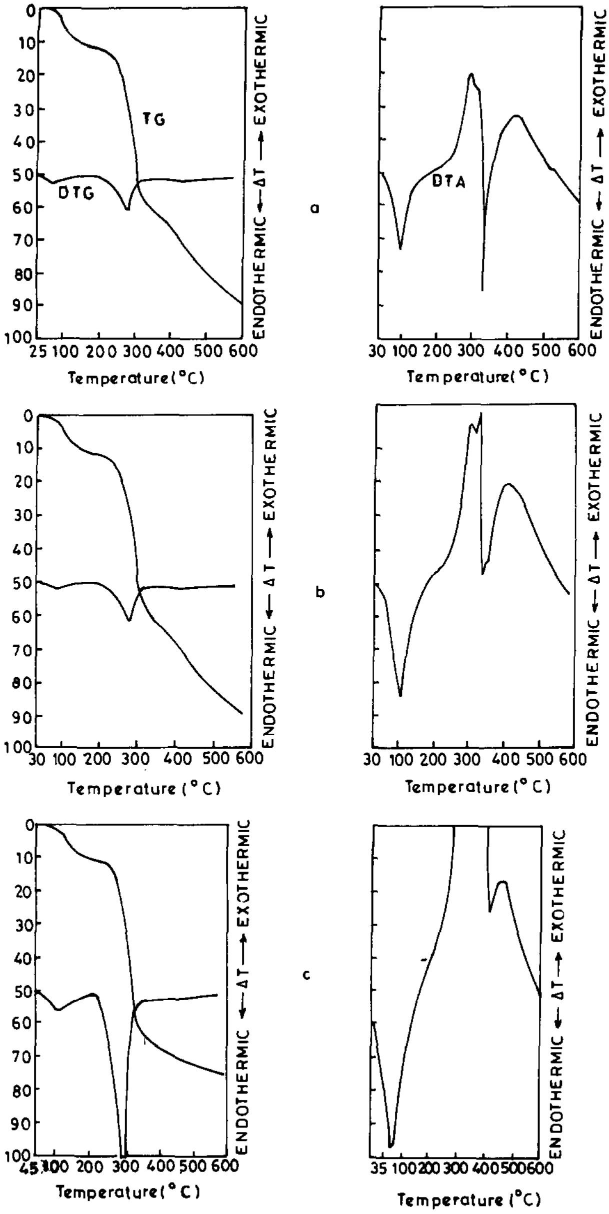

Fig. 3. TG, DTG and DTA analyses of the TMAA esters at heating rates of (a) 5, (b) 10 and (c) 20°C $\min^{-1}$.

represent the decomposition of unmodified cellulose moieties. At high heating rate and in the high temperature zone, the endothermic peak disappears. The exothermic decomposition process occurring over a wide range of temperature is attributable to oxidative attack at the C=O group by the C–H groups of cellulose. At a heating rate of 20°C $\min^{-1}$, the first

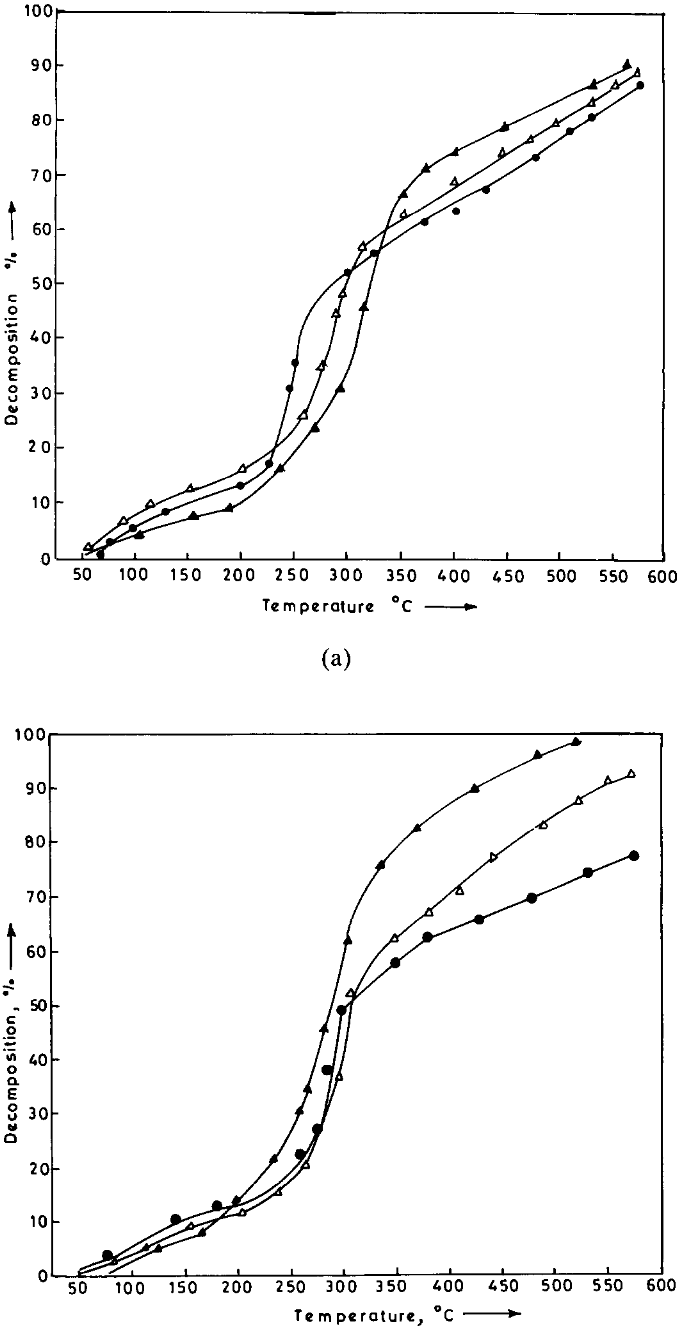

Fig. 4. (a) Thermograms of esterified products at a heating rate of 5°C min^{-1}: ●, TMA ester; △, PTA ester; ▲, TMAA ester. (b) Thermograms of esterified products at a heating rate of 10°C min^{-1}: ●, TMA ester; △, PTA ester; ▲, TMAA ester.

TABLE 1A

DTA data

Sample	DTA peak temperature (°C)											
	5°C min^{-1}				10°C min^{-1}				20°C min^{-1}			
	I	II	III	IV	I	II	III	IV	I	II	III	IV
TMA ester	73 (endo)	316 (exo)	362 [a] (endo)	432 [a] (exo)	89 (endo)	316 (exo)	392 (endo)	445 (exo)	116 (endo)	296 [b] (exo)	350 [b] (exo)	–
PTA ester	84 (endo)	290 (exo)	325 (endo)	425 (exo)	100 (endo)	332 (exo)	400 (exo)	–	94 (endo)	300 (exo)	425 (exo)	–
TMAA ester [c]	68 (endo)	280 (exo)	332 (endo)	392 (exo)	76 (endo)	292 (exo)	345 (endo)	410 (exo)	–	320 (exo)	400 (endo)	470 (exo)

TABLE 1B

DTG data

Sample	DTG peak temperature (°C)								
	5°C min^{-1}			10°C min^{-1}			20°C min^{-1}		
	I	II	III	I	II	III	I	II	III
TMA ester	77.5 (endo broad)	264 (endo)	–	73 (endo)	248 (endo)	–	94 (endo)	254 (endo) –	–
PTA ester	70 (endo)	272 (endo)	424 [d] (endo)	60 (endo)	272 (endo)	416 [e] (endo)	104 (endo)	292 (endo)	–
TMAA ester	75 (endo)	300 (endo)	–	68 (endo)	276 (endo)	–	92 (endo)	300 (endo)	–

TABLE 1C

Active decomposition temperature and weight loss

Sample	Weight loss (%)[f]									Active decomposition temperature (°C)								
	5°C min^{-1}			10°C min^{-1}			20°C min^{-1}			5°C min^{-1}			10°C min^{-1}			20°C min^{-1}		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
TMA ester	10 (25–162)	75 (162–600)	–	9.5 (25–140)	70.05 (140–600)	–	10.0 (30–174)	66 (174–600)	–	250	310	–	240	286	–	236	274	–
PTA ester	12 (25–164)	51 (164–374)	26 (374–600)	12 (25–164)	50 (164–340)	28 (340–600)	11 (25–208)	67 (208–600)	–	250	308	416	240	300	384	294	342	–
TMAA ester	8 (25–148)	82 (148–600)	–	7 (25–132)	82 (132–400)	–	5 (125–140)	83 (140–600)	–	250	332	–	248	315	–	250	340	–

[a] Close and fast occurring decomposition processes. [b] Close. [c] Quick change of peak above 200°C. [d] Broad and small. [e] Small. [f] Temperature range (in °C) in parentheses.

Key: I, II, III represent pre-, second and third stages.

endothermic peak is very steep, covering a wide range of temperatures (25–174°C), indicating loss of free moisture and bound water via an oxidative dehydration mechanism.

The DTA curve of the PTA ester (particularly at 5°C min^{-1}) exhibits similar trends with marginal differences in peak temperatures. This may be considered reasonable because both the esters are structurally identical with one additional CO and one additonal OH functional group in the case of the PTA ester. However, at high heating rates, i.e. 10 and 20°C min^{-1}, the endothermic peak tends to vanish beyond 200°C, the observation being more pronounced at 20°C min^{-1}. This would lead us to believe that the decomposition pathway changes when the heating rate is increased. Although the patterns of the DTA curves for TMAA at 5 and 10°C min^{-1} are similar in nature, at 20°C min^{-1} the low temperature endothermic peak disappears, indicating either the fast release of moisture or the simultaneous occurrence of moisture release and decomposition of the substituted ester group. The exotherm at 280–290°C is representative of oxidative attack of the CO group with the available CH groups. A fast endothermic peak at a temperature of around 320°C represents the melting and rapid degradation of cellulose. The exothermic process which followed immediately may be attributed to slow oxidation and evaporation or carbonization of the degraded fragments of the decomposed product. The char yield in the case of PTA is the lowest, indicating almost complete oxidation of the organic matter.

The TG and DTG curves of TMA show a major weight loss, with maxima at 264, 248 and 254°C, corresponding to heating rates of 5, 10 and 20°C min^{-1} respectively. The overall percentage weight loss decreases with increase of heating rate. In the case of PTA esters, two major weight loss steps can be seen with respective DTG maxima of 272 and 410°C corresponding to the active temperature of decomposition. However, at a heating rate of 20°C min^{-1}, only one major weight loss step is observed and the overall weight loss is also the lowest. Thus the decomposition pathway changes at a high heating rate.

TG and DTG of the TMAA ester exhibit one major weight loss step, the DTG maximum occurring at 300°C, which falls below the temperature of active decomposition. The initial temperatures at which the main decomposition step start are almost identical for all the heating rates and are comparable to those reported for cellulose esters derived from acetic anhydride [13].

Kinetic parameters

The retrieval of kinetic parameters from weight loss versus temperature data can be carried out by using various methods [21–35]. Modified versions of the well known Coats and Redfern [33] technique have been found to be the easiest and most reliable for retrieving kinetic parameters from dynamic thermogravimetry. Careful examination of the results obtained by various authors of kinetic parameters by various methods reveals that the Coats and Redfern technique can give the highest value for the correlation coefficient (R') and the lowest value of the minimum average deviation (%AAD) in linear least square fit of the deterministic functions. In view of this, the Coats and Redfern method has only been used to evaluate the values of the activation energy ΔE (kJ mol^{-1}) and frequency factor A (s^{-1}). The general correlation equation used in the Coats and Redfern method is

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

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). A computer program in Fortran was used for the linear least square analysis and applied to evaluate n, ΔE and A simultaneously. The procedure basically involves stepwise change of the order of the reaction n (over a range 0.5–2.0) to determine the correlation coefficient R' and %AAD in the least square estimate of the parameters ΔE and A. Table 2 shows the results of such computation for the main decomposition steps only. Although a satisfactory fit of the data can be realized over a range of reaction orders, an optimum value of 1 can be selected considering the distinguishable inflection points in the observed patterns of change of R' and %AAD. The activation energy required for decomposition of the TMA ester is the highest and conforms to the high thermal stability of this ester compared to the others.

The results presented in Table 2 indicate that kinetic compensation laws [36] as given by the equation $\log A = a + bE$ can be applied to the thermal decomposition of the esters over several runs at different heating rates. The values of the compensation parameters a and b for all the esters fall in the region of 3 s^{-1} and 5.3×10^{-3} mol kJ^{-1} s^{-1} respectively, with standard deviation of ±20%.

CONCLUSIONS

(1) Homogeneous esterification of cellulose with trimellitic acid anhydride (TMA), phthalic anhydride (PTA) and trimethyl acetic anhydride (TMAA) gives esters with appreciable degrees of esterification.

(2) The esters may be grouped according to decreasing thermal stability in the order TMA > PTA > TMAA.

(3) The thermal decomposition process conforms to first-order kinetics.

(4) The activation energies required for the decomposition of the esters are relatively higher than those reported for other cellulose esters.

TABLE 2

Kinetic parameters for the decomposition of the cellulose esters (shown at various values of n)

Sample	Order of reaction n	5°C min^{-1}				10°C min^{-1}				20°C min^{-1}			
		ΔE (kJ mol^{-1})	A (s^{-1})	%AAD	R'	ΔE (kJ mol^{-1})	A (s^{-1})	%AAD	R'	E (kJ mol^{-1})	A (s^{-1})	%AAD	R'
TMA ester	0.6	300.20	6.1×10^4	0.0061	0.99	313.84	7.4×10^4	0.0497	0.9857	482.80	2.27×10^5	0.0129	0.9946
	0.8	306.20	6.6×10^4	0.0092	0.993	302.14	6.6×10^4	0.0518	0.9818	492.27	2.43×10^5	0.0063	0.9955
	1.0	308.11	6.8×10^4	0.0123	0.993	289.02	5.95×10^4	0.0531	0.9710	502.30	2.56×10^5	0.0018	0.9950
	1.2	308.11	6.9×10^4	0.016	0.993	275.24	5.25×10^4	0.0537	0.970	501.60	2.58×10^5	0.0079	0.9963
	1.4	305.96	6.89×10^4	0.020	0.9937	261.57	4.59×10^4	0.0538	0.960	497.30	2.55×10^5	0.0130	0.9960
	1.6	301.19	6.6×10^4	0.022	0.9940	248.21	3.90×10^4	0.0540	0.950	490.60	2.44×10^5	0.0180	0.9960
PTA ester	0.6	200.23	1.78×10^4	0.0685	0.909	293.07	5.7×10^4	0.0715	0.960	341.50	9.2×10^4	0.0872	0.956
	0.8	198.80	1.83×10^4	0.0586	0.892	294.50	5.9×10^4	0.0680	0.959	331.98	8.6×10^4	0.0843	0.950
	1.0	194.98	1.78×10^4	0.055	0.898	292.84	5.97×10^4	0.067	0.9529	320.52	8.03×10^4	0.0822	0.954
	1.2	189.73	1.68×10^4	0.053	0.897	289.26	5.86×10^4	0.067	0.959	308.80	7.3×10^4	0.0820	0.957
	1.4	183.53	1.54×10^4	0.0539	0.870	284.48	5.68×10^4	0.066	0.952	296.80	6.7×10^4	0.0830	0.930
	1.6	176.84	1.38×10^4	0.054	0.860	278.75	5.43×10^4	0.0668	0.960	285.44	6.1×10^4	0.0880	0.923
TMAA ester	0.6	215.04	2.4×10^4	0.755	0.935	249.88	3.8×10^4	0.0786	0.931	258.15	4.07×10^4	0.0668	0.9584
	0.8	219.48	2.47×10^4	0.758	0.935	245.82	3.74×10^4	0.0736	0.924	252.46	3.88×10^4	0.0639	0.9536
	1.0	213.00	2.47×10^4	0.757	0.925	240.33	3.56×10^4	0.0702	0.917	245.49	3.63×10^4	0.0612	0.958
	1.2	214.46	2.4×10^4	0.770	0.922	234.64	3.35×10^4	0.068	0.910	237.70	3.35×10^4	0.0610	0.952
	1.4	206.35	2.3×10^4	0.776	0.910	231.70	3.1×10^4	0.066	0.910	239.70	3.40×10^4	0.059	0.933
	1.6	201.90	2.2×10^4	0.780	0.910	219.42	2.84×10^4	0.065	0.900	221.40	2.43×10^4	0.059	0.933

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