Thermal Behavior of Cellulosic Graft Copolymers. I. Cotton Grafted with Vinyl Acetate and Methyl Acrylate

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Synopsis

The thermal degradation of samples of cotton, cotton oxidized by ceric ion, cotton grafted with vinyl acetate and methyl acrylate having different percent grafting yield, poly(vinyl acetate), and poly(methyl acrylate) has been investigated using the techniques of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in nitrogen. The kinetic parameters E, n, and A have been obtained following several methods of thermogravimetric analyses. The ceric ion redox system shows little effect upon thermic properties of cotton cellulose. Graft copolymerization of vinyl acetate makes cotton thermally less stable, while, in the case of methyl acrylate grafted cotton samples having 33, 83, and 174% grafting yield, the initial decomposition starts at lower temperatures; but decomposition beyond 360°C takes place at higher temperatures than those for ungrafted cotton, and in the case of the sample with 430% grafting yield the thermal stability is higher than that of original cotton. The thermal stability of cotton grafted with methyl acrylate is higher than that of cotton grafted with vinyl acetate. The degradation of cellulose and cellulose graft copolymers is complex as is shown by DTA thermograms and kinetic parameters.

INTRODUCTION

Modification of cellulose fibers by graft copolymerization with various monomers is considered to be very effective in bringing about desired changes in the properties of cellulose fibers. Many authors have attempted to graft-copolymerize cellulose using different initiators,[1-3] but only few workers have tested the thermal stability of the grafted fibers[4-8] and the effect of the redox initiator on thermal properties of cellulose.[9]

The thermogravimetric analysis (TGA) is widely used as a method to investigate the thermal decomposition of polymers and to determine some kinetic parameters such as activation energy E and order of reaction, n. The values of these parameters can be of major importance in the elucidation of the mechanisms involved in polymer degradation and in the estimation of the thermal stability of polymers.

In the present study the thermal degradation of cotton cellulose, cotton cellulose oxidized by ceric ion (ceric ammonium nitrate) and cotton cellulose grafted with vinyl acetate and methyl acrylate in nitrogen has been investigated using DTA and TGA techniques.

EXPERIMENTAL

Samples

The following samples of cellulose and cellulose grafted with vinyl acetate and methyl acrylate were selected for the present work.

Sample (i), cotton purified[10] and dried over phosphorous pentoxide with a number-average molecular weight of 226, 136; sample (ii), cotton oxidized by ceric ion (ceric ammonium nitrate) under identical conditions as those in the grafting reaction[11] (ceric ion concentration: $5 \times 10^{-3}N$, reaction time: 6 h), and dried over phosphorous pentoxide, with a number-average molecular weight of 201, 187; samples (iii–v), cotton grafted with vinyl acetate (cellulose-g-PVA) using ceric ion as initiator[11] and with a grafting yield of 18, 67, and 89%, respectively; samples (vi–ix), cotton grafted with methyl acrylate (cellulose-g-PMA) using ceric ion as initiator[11] and with a grafting yield of 33, 83, 174, and 430%, respectively; sample (x), poly(vinyl acetate) (PVA) obtained as homopolymer in the grafting reaction; sample (xi), poly(methyl acrylate) (PMA) obtained as homopolymer in the grafting reaction.

Thermogravimetric (TG) and Derivative Thermogravimetric Analyses (DTGA)

The TG and DTG thermograms were obtained using a DuPont 951 TGA attached to a DuPont 990 thermal analyzer. Samples of about 12 mg were degraded in a dynamic nitrogen atmosphere at different heating rates ranging from 2 to 20°C/min.

Differential Thermal Analysis (DTA)

The differential thermal analysis curves were obtained from a DuPont DTA base module II attached to a DuPont 990 thermal analyzer. The DTA curves were run under dynamic nitrogen atmosphere at a heating rate of 20°C/min. Glass beads were taken as reference material.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Figure 1 shows dynamic TGA and DTGA curves of purified cotton and oxidized cotton. Thermal decomposition of cotton takes place in two distinct stages in the temperature range 150–600°C. In the first stage, temperature range 260–400°C, most of the decomposition of cellulose takes place. During the second stage, temperatures > 400°C, undecomposed cellulose and other impurities which amount to about 20% of the total weight are lost.

Table I summarizes the temperature at which the weight loss reaction began (T_i), the temperature of maximum pyrolysis (T_m), percent residue for the reaction found at the cessation of rapid loss in sample weight, and percent char at 500°C.

The decomposition of both cotton samples begins at the same temperature. However, the maximum rate of cellulose pyrolysis occurred at 369° and 363°C for purified cotton and oxidized cotton, respectively as the differential TGA
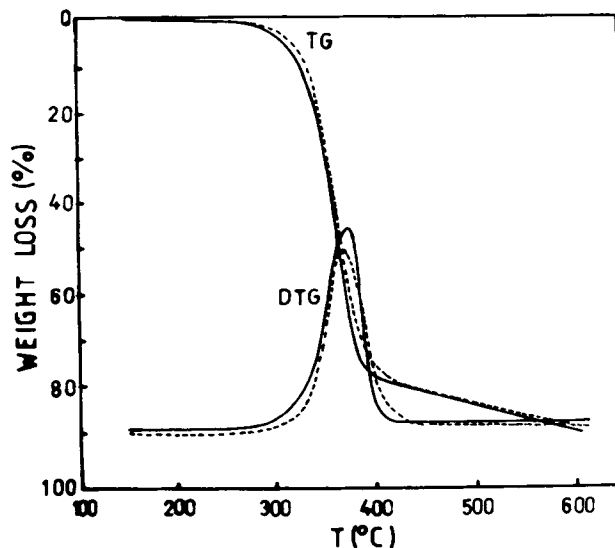
Fig. 1. TGA and DTGA curves of cotton: (—) purified; (---) oxidized. Heating rate = 10°C/min.

TABLE I
Effect of Ceric Ion Redox System on the Thermal Decomposition of Cotton Cellulose

Sample	T_i (°C)	T_m (°C)	Residue (%)	Char (%)
Cotton oxidized by $(NH_4)_2Ce(NO_3)_6$	261	363	23.7	16
Original purified cotton	261	369	22.2	15.5

curves show. The percent residue and percent char are similar for both cellulose samples.

Table II shows the decomposition temperatures (T_D) at different weight losses for both cotton samples Comparing T_D at different weight losses, the stability of both cotton samples differs slightly, being the decomposition temperatures of oxidized cotton greater than those of purified cotton. These results are in agreement with those reported by Luzakova et al.[9] since they

TABLE II
Temperature of Decomposition at Different Weight Losses of Purified Cotton
and Cotton Oxidized by Ceric Ammonium Nitrate

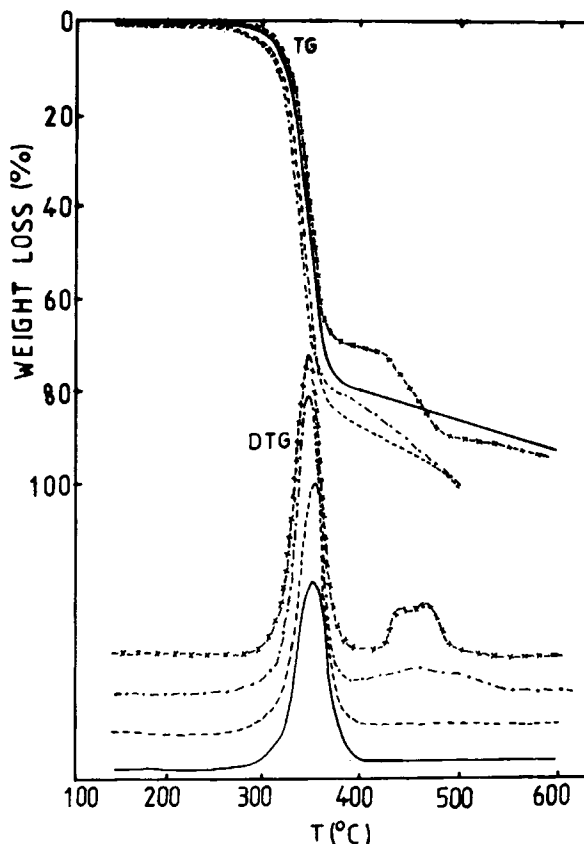| Sample	Temperature of decomposition (°C) at weight loss of							
	10%	20%	30%	40%	50%	60%	70%	80%
Purified cotton	326	342	351	357	363	369	377	414
Oxidized cotton	333	346	353	360	367	374	385	421

Fig. 2. TGA and DTGA curves of cotton grafted with vinyl acetate and poly(vinyl acetate); (-··-) 18% grafting yield; (---) 67% grafting yield; (—) 89% grafting yield; (-×-) PVA. Heating rate = 10°C/min.

found that when ceric salts are used as redox initiators in relatively low concentration, only very small amounts of the inorganic salts were adsorbed on cellulose and these did not affect significantly the course of thermooxidative decomposition: but the presence of NH_4 cations was favorable.

Figure 2 shows dynamic TGA and DTGA curves of cellulose-g-PVA and PVA. As can be seen, the pyrolysis of cellulose-g-PVA samples takes place in two steps from 150 to 550°C. In the first stage, temperature range 260–380°C, most of the decomposition of cellulose graft copolymer takes place. During the second stage, temperatures > 380°C, about 15–20% of the total weight of graft copolymer is lost. On the other hand, the decomposition of PVA takes place in two main stages with different rates as it is obvious from DTGA curve. In the first stage, temperature range 280–380°C, the most decomposition of the polymer takes place. During the second step, temperature range 410–530°C, the 30% of sample weight is decomposed.

Table III shows T_i, T_m, percent residue, and percent char for cellulose-g-PVA, PVA, and ungrafted cellulose. The decomposition of cellulose-g-PVA samples begins at the same temperature of that of ungrafted cotton, but at lower temperature than PVA does. T_m values increase slightly with increasing

TABLE III
Thermal Analytical Data for Cotton Grafted with Vinyl Acetate

Sample	Grafting yield (%)	T_i (°C)	T_m (°C)	Residue (%)	Char (%)
Vinyl acetate-grafted cotton	18	261	343	21	0
	67	261	351	17	0
	89	261	352	21	14
PVA	—	280	343[a]	10	8.7
Purified cotton	—	261	369	22.2	15.5
Oxidized cotton	—	261	363	23.7	16

[a] T_m value for the first step.

percent grafting yield of copolymer. T_m values of copolymers are lower than that of ungrafted cotton but higher than T_m for the first step of PVA. These results indicate that the degradation of graft copolymers is different from that of PVA.

The percent residue for cellulose graft copolymers is lower than that for both PVA and ungrafted cotton. Char was not observed for cellulose-*g*-PVA samples with 18% and 67% grafting yield, while the percent char for cellulose-*g*-PVA sample with 89% grafting yield is higher than that for PVA but slightly lower than that for ungrafted cellulose.

Figure 3 shows the temperature dependence of the degree of conversion for cellulose-*g*-PVA, PVA, and ungrafted cellulose. Temperature values for the
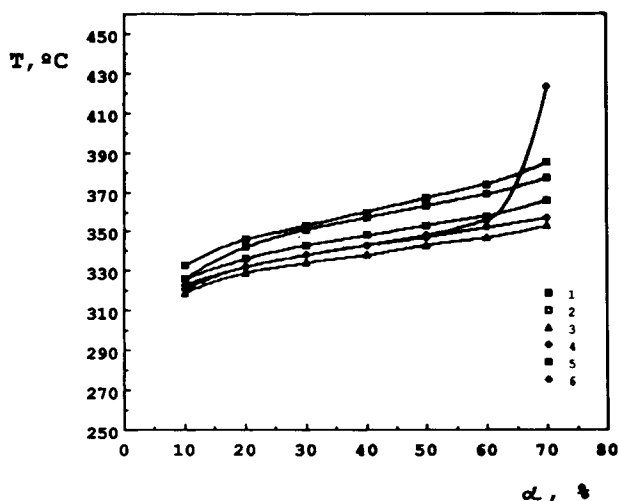

Fig. 3. Temperature dependence of the degree of conversion for cotton grafted with vinyl acetate comparatively with the initial cotton and poly(vinyl acetate): (1) purified cotton; (2) oxidized cotton; (3) grafted cotton 18% grafting yield; (4) grafted cotton 67% grafting yield; (5) grafted cotton 89% grafting yield; (6) PVA.
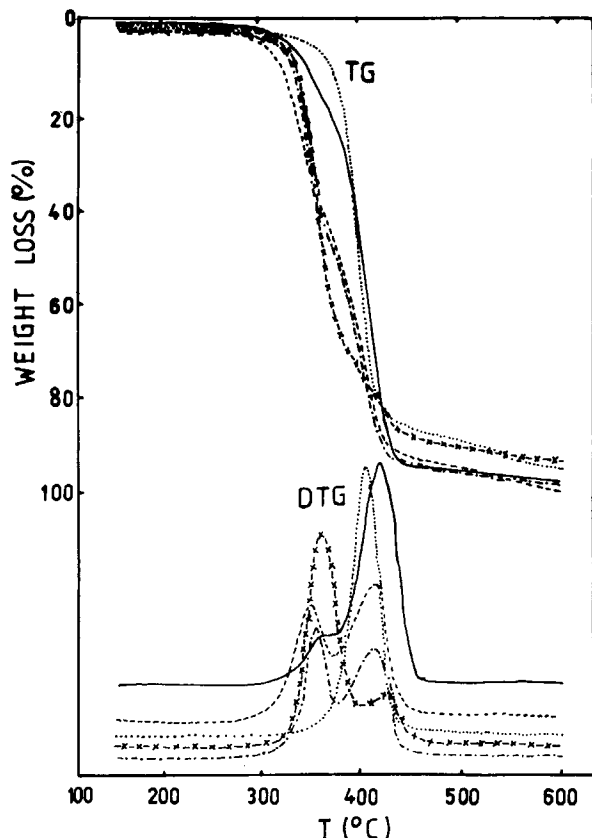
Fig. 4. TGA and DTGA curves of cotton grafted with methyl acrylate and poly(methyl acrylate): (- ×-) 33% grafting yield; (---) 83% grafting yield; (---) 174% grafting yield; (—) 430% grafting yield; (···) PMA. Heating rate = 10°C/min.

graft copolymers increase continuously as percent grafting yield increases from 18 to 89%. Temperature values for cellulose-g-PVA samples are lower than those for ungrafted cotton. Temperature values for cellulose-g-PVA sample with 89% grafting yield are higher than those of PVA, while those values for cellulose-g-PVA sample with a grafting yield of 67% are roughly similar to those of PVA up to 60% conversion. However, in the case of the graft copolymer sample with 18% grafting yield, the temperature values are lower than those of PVA.

From these results it can be concluded that grafting of vinyl acetate onto cellulose imparts a decrease in thermal stability of cellulose. The results also show that thermal stability of graft copolymers increases with the increase in percent grafting yield, and the stability of graft copolymers is higher than that of PVA in the case of samples with grafting yield higher than 67%, while thermal stability of samples with grafting yield lower than 67% is lower than that of PVA.

Figure 4 shows dynamic TGA and DTGA curves of cellulose-g-PMA and PMA. As can be seen, the pyrolysis of cellulose-g-PMA takes place in three steps with different rates, in the temperature range 150–550°C. In the first

TABLE IV
Thermal Analytical Data for Cotton Grafted with Methyl Acrylate

Sample	Grafting yield (%)	T_i (°C)	$T_{m\,I}$[a] (°C)	$T_{m\,II}$[b] (°C)	Residue (%)	Char (%)
Methyl acrylate-grafted cotton	33	266	357	420	9.5	8.3
	83	259	350	410	8.4	8.3
	174	246	345	412	9.6	7.6
	430	283	357	416	7.2	5.6
PMA	—	314	402	—	18	11
Purified cotton	—	261	369	—	22.2	15.5
Oxidized cotton	—	261	363	—	23.7	16

[a] T_m value for the first step.
[b] T_m value for the second step.

stage, temperature range 240–310°C, the cellulose-g-PMA sample with 33% grafting yield loses the 75% of sample weight, whereas cellulose-g-PMA samples with a grafting yield of 83, 174, and 430% lose the 50, 45, and 20% of sample weight, respectively. During the second stage, temperature range 310–460°C, the most of the decomposition of cellulose-g-PMA sample with 430% grafting yield takes place (75% weight loss), while cellulose-g-PMA samples with 33, 83, and 174% grafting yield lose the 15, 40, and 45% of sample weight, respectively. The decomposition of PMA takes place in one step in the temperature range 314–419°C with 80% weight loss.

Table IV shows T_i, T_m, percent residue, and percent char for cellulose-g-PMA, PMA, and ungrafted cellulose. The decomposition of cellulose-g-PMA samples with 83 and 174% grafting yield begins at a lower temperature than that of both ungrafted cotton and PMA, while the decomposition of cellulose-g-PMA samples with 33 and 430% grafting yield begins at a higher temperature than that of ungrafted cellulose but at lower one than that of PMA.

T_m values for the first step of decomposition of graft copolymers are lower than the T_m value of both ungrafted cotton samples and PMA. T_m values for the second step of decomposition of graft copolymers are higher than the T_m value of both PMA and ungrafted cotton. These results indicate that the degradation of graft copolymers (cellulose-g-PMA) is different from that of PMA.

The percent residue for cellulose-g-PMA is lower than that for both ungrafted cotton and PMA. The percent residue is roughly similar for the four graft copolymer samples. The percent char for cellulose graft copolymers decreases with an increase in percent grafting yield. The percent char for graft copolymers are lower than that of both PMA and ungrafted cellulose.

Figure 5 shows the temperature dependence of the degree of conversion for cellulose-g-PMA, PMA, and ungrafted cotton. The values of temperature at 10, 20, and 30% decomposition for the graft copolymers decrease on increasing percent grafting yield from 33 to 174%, but increase on further increase of percent grafting yield. However, temperature values at 40, 50, 60, and 70% conversion increase with an increase in percent grafting yield.
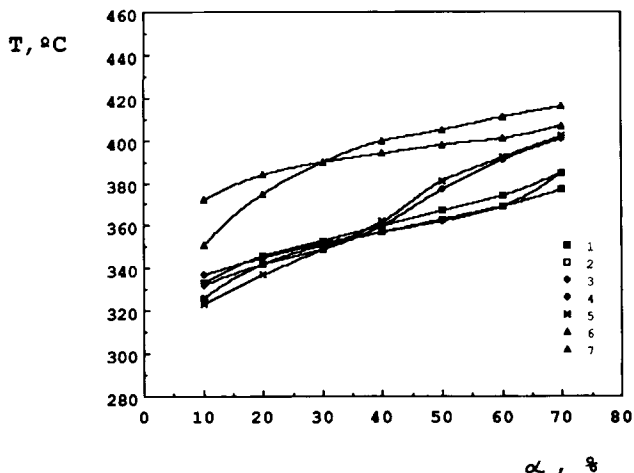
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Fig. 5. Temperature dependence of the degree of conversion for cotton grafted with methyl acrylate comparatively with the initial cotton and poly(methyl acrylate): (1) purified cotton; (2) oxidized cotton; (3) grafted cotton 33% grafting yield; (4) grafted cotton 83% grafting yield; (5) grafted cotton 174% grafting yield; (6) grafted cotton 430% grafting yield; (7) PMA.

Temperature values for cellulose-g-PMA samples having 33, 83, and 174% grafting yield are lower than those for ungrafted cotton up to a conversion of 40%; beyond that, degree of conversion temperature values for the graft copolymers having 83 and 174% grafting yield are higher than those for ungrafted cotton, while temperature values for the sample having 33% grafting yield are roughly similar to those of ungrafted cotton.

Temperature values for graft copolymer sample with 430% grafting yield are higher than those of ungrafted cotton. Temperature values for graft copolymers are lower than those for PMA, but in the case of the sample having 430% grafting yield temperature values beyond a conversion of 30% are higher than those for PMA.

From these results it can be concluded that the effect of grafting of methyl acrylate onto cellulose on the thermal stability of cellulose depends on the percent grafting yield. The cellulose graft copolymer having 430% grafting yield has a higher thermal stability than that of ungrafted cellulose, while in the case of cellulose graft copolymers having 33, 83, and 174% grafting yield, although decomposition commences at comparatively lower temperatures as compared with cotton, grafting of methyl acrylate results in a delay in the decomposition of cellulose beyond 360°C.

The thermal stability of graft copolymers decreases with an increase in percent grafting yield up to a certain value of grafting yield beyond which stability increases. The stability of graft copolymers is lower than that of PMA.

Figure 6 shows the temperature dependence of the degree of conversion for cellulose-g-PVA and cellulose-g-PMA. As can be seen, temperature values for cellulose-g-PMA samples are higher than those for cellulose-g-PVA. From these results it can be concluded that the thermal stability of cotton grafted with methyl acrylate is higher than that of cotton grafted with vinyl acetate.
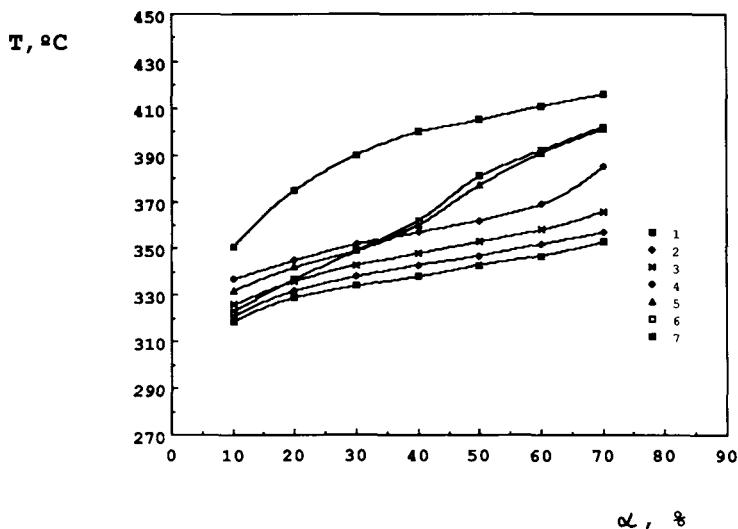
Fig. 6. Temperature dependence of the degree of conversion for cotton grafted with vinyl acetate comparatively with cotton grafted with methyl acrylate: (1) VA grafted cotton 18% grafting yield; (2) VA grafted cotton 67% grafting yield; (3) VA grafted cotton 89% grafting yield; (4) MA grafted cotton 33% grafting yield; (5) MA grafted cotton 83% grafting yield; (6) PMA grafted cotton 174% grafting yield; (7) MA grafted cotton 430% grafting yield.

This is probably due to the higher thermal stability of PMA as compared with that of PVA as it is shown in Figure 7.

Hurduc et al[8] obtained similar results in their study on thermal properties of grafted cellulose; they pointed out that the thermal stability of natural cellulose is greater than that of grafted cellulose. However, Varma and Narasimhan[6] found that the thermal stability of cellulose grafted with methyl acrylate is higher than that of natural cellulose.
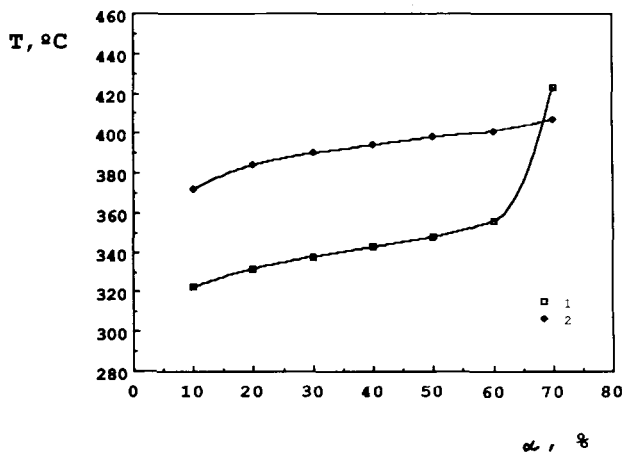
Fig. 7. Temperature dependence of conversion for poly(vinyl acetate) and poly(methyl acrylate): (1) PVA; (2) PMA.

Calculation of Kinetic Parameters

In order to calculate the kinetic parameters from TG curves, the method of Friedman,[12] Kissinger,[13] Flynn and Wall,[14] and Reich[15] were used. The equations involved in Friedman [eqs. (1)–(2)], Kissinger [eq. (3)], Flynn–Wall [eq. (4)], and Reich [eq. (5)] methods can be written as

$$\ln[B(d\alpha/dT)] = \ln R_t = \ln A + \ln f(\alpha) - E/RT \tag{1}$$

$$f(\alpha) = (1 - \alpha)^n \tag{2}$$

$$-\frac{d(\ln B/T_m^2)}{d(1/T_m)} = -\frac{E}{R} \tag{3}$$

$$-\frac{d \log(B)}{d(1/T)} = 0.457 \frac{E}{R} \tag{4}$$

$$\ln(B/T^2) = -E/RT + \ln[AR/E(\text{const})] \tag{5}$$

where B is the constant rate of heating (°C/min), R_t is the rate of chemical reaction, α is the degree of conversion, A is the preexponential (frequency) factor, E is energy of activation, n is reaction order, and T_m maximum temperature on DTG curve.

According to the method of Friedman, a plot of $\ln[B(d\alpha/dT)]$ vs. $1/T$ was made. The values of T at constant α were taken from curves obtained at different heating rates. Thus a family of straight lines was obtained whose slope is E/R and whose intercept is $\ln[Af(\alpha)]$. By plotting $\ln[Af(\alpha)]$ vs. $\ln(1 - \alpha)$, both preexponential factor and reaction order were obtained. In this manner, average values of E and A were obtained over a range of conversion. The series of curves obtained indicate the conversion at which the pyrolysis kinetics begin to vary.

The Kissinger method allows calculation of activation energy from one point (maximum on DTG curve) at several heating rates. The energy of activation was obtained from the slope of a plot of $\ln(B/T_m^2)$ vs. $1/T_m$.

The method of Flynn and Wall requires several curves at different heating rates. The energy of activation was obtained from the slope of a plot of $\log B$ against $1/T$. This procedure was repeated at various degrees of conversion to test the constancy of E with respect to conversion.

The method of Reich also requires use of more than two thermograms obtained at different heating rates. Various specific values of α were chosen and $\ln[B/T^2]$ was plotted vs. $1/T$; a series of lines were obtained whose slopes gave values of E. Values of E were obtained at various conversions to determine whether any change in mechanism is occurring as conversion changes.

Figure 8 shows the TGA and DTGA curves for cellulose-g-PMA at different heating rates. Note that the curves are displaced to higher temperatures with increasing heating rate, as would be predicted from kinetic theory. The above-mentioned methods were applied to each stage separately.
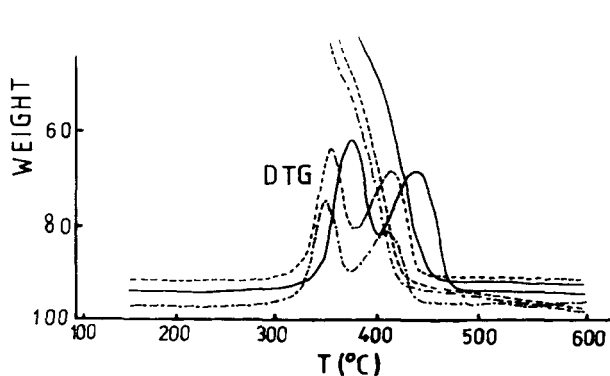
Fig. 8. TGA and DTGA curves for cotton grafted with methyl acrylate (83% grafting yield) at various heating rates (°C/min): (-··-) 5; (---) 10; (—) 20.

TABLE V
Kinetic Characteristics of the Thermal Degradation of Cellulose, Cellulose Grafted with Vinyl Acetate and Methyl Acrylate, Poly(vinyl Acetate), and Poly(methyl Acrylate)

Sample	Grafting yield (%)	α (%)	E (Kal/mol)				Friedman		
			Friedman	Kissinger	Flynn–Wall	Reich	α (%)	n	A (min^{-1})
Purified cotton	—	10–70	47.1	30	40	39	10–45	0.3	5.3×10^{16}
							50–70	1	1.1×10^{17}
Oxidized cotton	—	10–70	36.4	36.7	55.5[a]	56[a]	10–40	0	6.5×10^{12}
							50–70	1.4	2.3×10^{13}
VA-grafted cotton	18	5–50	28.9	33.3	43.5	43.4	10–50	0	3.4×10^{10}
	67	5–50	37	36.4	39.8	39.5	10–50	0	3.5×10^{13}
	89	30–60	46.7	42.3	44	44	30–60	2.2	1.3×10^{17}
MA-grafted cotton	33	5–75	25	27.5	29	27.4	15–45	0	1.3×10^{9}
							47–75	1	3.6×10^{9}
		75–90	—	23.5	24	22.6	—	—	—
	83	5–50	38.8	40.8	41	43.2	10–30	0	5.3×10^{13}
							30–50	1	1.4×10^{14}
		55–90	40.2	32.3	39	38.5	60–90	1	1.2×10^{13}
MA-grafted cotton	174	10–45	45.1	33	47	47.5	20–45	1	2.1×10^{16}
		50–90	36.7	37.4	42	41.3	50–90	0	1.1×10^{12}
	430	10–60	27.2	26	28.3	27.2	10–60	0	9.2×10^{8}
PVA	—	5–60	42.3	43.6	53	53.4	10–60	0	2.2×10^{15}
PMA	—	30–70	44.4	32.7	77.7[a]	79.1[a]	30–70	0.6	9.6×10^{14}
					51.3[b]	51.3[b]			

[a] $E_{a,0}$.
[b] Degree conversion range 55–80%.

TABLE VI
The Influence of the Transformation Degree on Activation Energy
of Oxidized Cotton and Poly(methyl Acrylate)

Sample	α (%)	Flynn–Wall		Reich	
		E (kcal/mol)	$E_{\alpha,0}$ (kcal/mol)	E (kcal/mol)	$E_{\alpha,0}$ (kcal/mol)
Oxidized cotton	10	54.5	55.5	55	56
	20	49		48.7	
	30	45.6		45.6	
	40	42.3		42.1	
	50	41		40.6	
	60	38		37.7	
	70	35.9		35.2	
PMA	10	73	77.7	74	79.1
	20	69		72	
	30	65		61.5	
	40	61		58.5	
	50	57		53.6	
	60	51.1		51	

The values of E, n, and A determined using the above-mentioned methods are given in Table V, for ungrafted cellulose samples (purified and oxidized cotton), cellulose graft copolymers (cellulose-g-PVA and cellulose-g-PMA), PVA, and PMA. These parameters have been evaluated using the method of least squares for all the methods.

Using the above-mentioned methods, we followed the influence of the transformation degree upon the activation energy. In the cases where E depends on the degree of conversion, the activation energy of the initiation step of the reaction, $E_{\alpha,0}$, was calculated by extrapolating the straight line obtained by plotting E vs. α.

The results shown in Table V indicate that two mechanisms of degradation are involved in the decomposition of cotton cellulose. The values of both activation energy and frequency factor obtained for cotton are in agreement with those obtained by Bradbury et al.[16] isothermally. The activation energy value (Friedman's method) for oxidized cotton is lower than that of purified cotton. The reaction orders are similar for both cotton cellulose samples, while frequency factor values are higher for purified cotton. Table VI shows the influence of the transformation degree on the activation energy for oxidized cotton. However, in the case of purified cotton, applying the Flynn–Wall and Reich's methods, we found that the degree of conversion did not affect the activation energy.

The activation energy obtained by Friedman's and Kissinger's methods for cellulose grafted with vinyl acetate increases with increasing percent grafting yield. The same trend is observed in frequency factor values, while reaction order changes from 0 to 2.2 when grafting yield increases from 67 to 89%.

Comparison of the cellulose graft copolymer samples with ungrafted cellulose shows that the activation energy (Friedman's method) was lower for cellulose grafted with vinyl acetate than for purified cotton. However, activation energy for cellulose-g-PVA sample having 18% grafting yield was lower

than that of oxidized cotton, while for the samples with higher percent grafting yield the value of activation energy is roughly similar to that of oxidized cotton. On the other hand, the values of activation energy for cellulose-g-PVA samples having 18 and 67% grafting yield are lower than that for PVA, whereas the E value for the sample having 89% grafting yield is roughly similar to that for PVA.

From the results shown in Table V it can be deduced that two mechanisms are involved in the first stage of pyrolysis of cellulose-g-PMA samples having 33 and 83% grafting yield. The energy of activation for the first stage of pyrolysis of cellulose-g-PMA increases with an increase in percent grafting yield up to a certain value of grafting yield beyond which the activation energy decreases. The energy values for the second stage of pyrolysis for those graft copolymers increase with increasing grafting yield.

The frequency factor of cellulose-g-PMA samples increases with increasing percent grafting yield up to a value of grafting yield beyond which the preexponential factor decreases. The reaction orders are similar for all graft copolymer samples. On the other hand, the values of activation energy for cellulose grafted with methyl acrylate are lower than that for both ungrafted cotton samples. The same trend is observed when the values of activation energy for those graft copolymers and PMA are compared.

From the results shown in Table V it can be deduced that more than one mechanism is involved in the pyrolysis of PMA. Table VI shows the influence of the transformation degree on the activation energy for PMA. The activation energy values for methyl acrylate grafted cotton samples (Table V) are of the same order as those reported by Varma and Narasimhan[6] and Sharma and Daruwalla.[7] The activation energy value for poly(vinyl acetate) is of the same order of that reported by Jellinek[17] and Vasile.[18]

Differential Thermal Analysis

The DTA thermograms of (i) purified cotton, (ii) oxidized cotton, (iii–v) vinyl acetate grafted cotton, (vi–ix) methyl acrylate grafted cotton, (x) poly(vinyl acetate), and (xi) poly(methyl acrylate) were recorded in the temperature range 60–460°C and are shown in Figures 9–12. The peak temperature for various endotherms are given in Table VII.

The DTA curve of purified cotton shows two endothermic peaks (Fig. 9). A small endotherm in the temperature range 80–182°C, followed by a deeper endotherm in the temperature range 315–395°C, split into two peaks with its respective peak minimum at 355 and 374°C. On the other hand, the DTA curve of oxidized cotton is similar to that of purified cotton, showing two endotherms. From Figure 9 and Table VII it is evident that, although the curve of oxidized cotton has the same shape as that of purified cotton, the peak minimum for the second endotherm takes place at a lower temperature, 351 and 368°C instead of 355 and 374°C.

The DTA curves of the graft copolymers cellulose-g-PVA, having different percent grafting yield, show two endotherms (Fig. 10), the first one in the temperature range 80–179°C, and the second one between 295 and 400°C. The peak minimum temperature is roughly similar for the three copolymer sam-
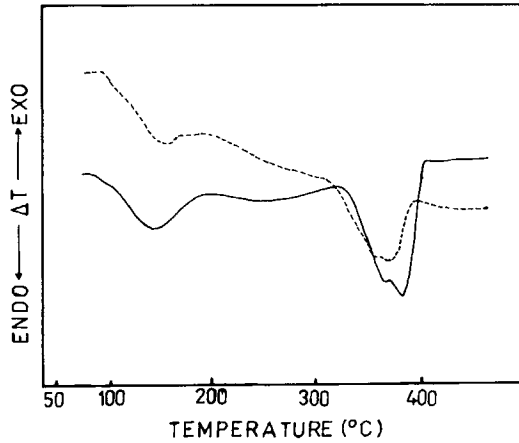
Fig. 9.   DTA thermograms of ungrafted cotton: (—) purified cotton; (---) oxidized cotton.
Heating rate = 20°C/min.

ples. The sample having 89% grafting yield shows a hump in the second
endotherm at about 383°C.

The DTA curves of the graft copolymers cellulose-g-PMA, with different
percent grafting yield, show three endothermic peaks (Fig. 11). The first one,
the smallest, is in the temperature range 80–190°C; the second one is in the
temperature range 305–397°C and the third one is between 393° and 466°C.
In the case of the copolymer sample having 33% grafting yield, the second
endotherm is the largest one, whereas, in the case of the samples having 83
and 174% grafting yield, the largest endotherm is the third one, the second
one being split into two peaks. In the DTA curve of the sample having 430%
grafting yield, instead of two distinct endotherms in the temperature range
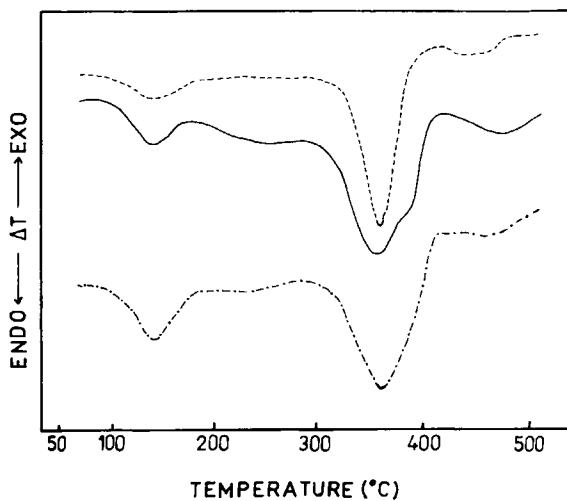

Fig. 10.   DTA thermograms of cotton grafted with vinyl acetate: (-··-) 18% grafting yield; (---)
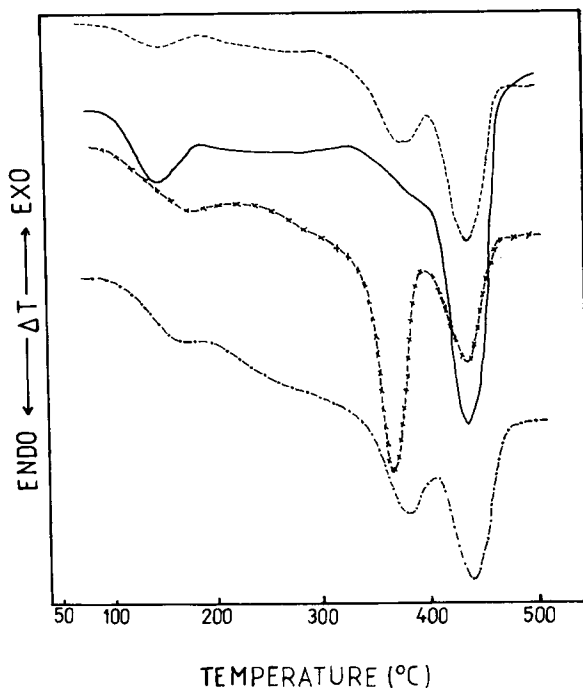67% grafting yield; (—) 89% grafting yield. Heating rate = 20°C/min.

Fig. 11.   DTA thermograms of cotton grafted with methyl acrylate: (– ×–) 33% grafting yield; (–··-) 83% grafting yield; (---) 174% grafting yield; (—) 430% grafting yield. Heating rate = 20°C/min.

305–466°C, a shoulder is observed in the temperature range 324–397°C. The peak minimum temperature is roughly similar for the four copolymer samples.

The DTA thermogram of PVA shows three distinctic endotherms (Fig. 12): the first one, the smallest, in the range 95–170°C, the second one between 290 and 388°C with its peak minimum at 340°C, showing a hump at about 374°C, and the third one appearing at a temperature higher than 426°C. The DTA curve of PMA shows two different endotherms (Fig. 12), the first one in the temperature range 100–210°C, and the second one in the range 365–455°C
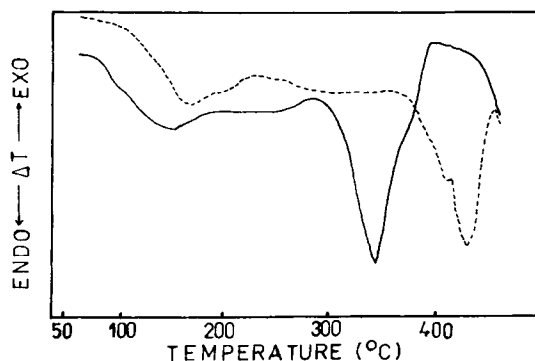

Fig. 12.   DTA thermograms of poly(vinyl acetate) and poly(methyl acrylate): (—) PVA; (---) PMA. Heating rate = 20°C/min.

TABLE VII
Peak Temperature in The DTA Thermograms for Cellulose, Cellulose Grafted with Vinyl
Acetate and Methyl Acrylate, Poly(vinyl Acetate), and Poly(methyl Acrylate)

Sample	Grafting yield (%)	Endotherm I Temp range (°C)	Endotherm II			Endotherm III		
			T_i (°C)	T_m (°C)	T_f (°C)	T_i (°C)	T_m (°C)	T_f (°C)
Purified cotton	—	80–812	317	355[a] 374[a]	395	—	—	—
Oxidized cotton	—	95–190	305	351[a] 368[a]	390	—	—	—
VA-grafted cotton	18	80–180	295	355	400	—	—	—
	67	80–180	314	355	391	—	—	—
	89	80–180	295	353	402	—	—	—
MA-grafted cotton	33	80–190	317	360	386	393	428	456
	83	80–190	321	374	397	400	431	466
	174	80–190	305	357[a] 369[a]	395	396	431	461
	430	80–190	329	—	—	—	433	464
PVA	—	95–170	290	340	388	—	—	—
PMA	—	100–210	365	422	455	—	—	—

[a] Endotherm splitted into two peaks.

with its peak minimum temperature at 422°C and with a hump at about 405°C.

From the above results it can be concluded that two mechanisms are involved in the pyrolysis of cellulose (purified and oxidized cotton) in the temperature range 300–390°C. The same conclusion was deduced from the kinetic data (Table V). On the other hand, it can be deduced that two mechanisms are also involved in the first stage of pyrolysis of graft copolymer samples, cellulose-g-PMA, having 83 and 174% grafting yield. In the case of PMA and PVA samples the results indicate that two mechanisms are also involved in the pyrolysis reaction. The same conclusions were deduced from the kinetic data (Table V).

CONCLUSIONS

Thermogravimetric analyses of purified cotton and cotton oxidized by ceric ion under nitrogen shows that the ceric ion redox system has only a slight effect on the course of thermal decomposition of cellulose. It results from our study that the thermostability of vinyl acetate grafted cellulose is lower than that of initial cellulose, and the thermal stability of graft copolymers increases with the increase in percent grafting yield.

On the other hand, the thermostability of methyl-acrylate-grafted cellulose is higher than that of ungrafted cellulose if the percent grafting yield of the graft copolymer is 430% whereas with the graft copolymers having a grafting yield between 33 and 174%, although decomposition starts at comparatively lower temperatures as compared with initial cellulose, grafting of methyl acrylate results in a delay in the decomposition of cellulose beyond 360°C. The thermal stability of the graft copolymers, cellulose-g-poly(methyl acrylate), decreases with an increase in percent grafting yield up to a certain value

of grafting yield beyond which stability increases. The thermostability of graft copolymers is lower than that of poly(methyl acrylate).

The thermal stability of methyl-acrylate-grafted cotton is higher than that of vinyl-acetate-grafted cotton, which is attributed to the lower thermal stability of poly(vinyl acetate) as compared to poly(methyl acrylate).

The DTA studies in nitrogen atmosphere indicate that the thermal degradation of cotton cellulose takes place via two endothermic processes. In the case of vinyl-acetate-grafted cotton, the decomposition takes place via an endothermic process, while, in the case of methyl-acrylate-grafted cotton, the pyrolysis reaction takes place via two or three endothermic processes, depending on percent grafting yield, indicating that the decomposition reaction of graft copolymers is quite complicated. DTA of poly(vinyl acetate) showed that the decomposition took place via three endothermic processes, while the curve of poly(methyl acrylate) showed two endothermic peaks.

The kinetic results and DTA studies showed that several mechanisms are involved in the pyrolysis of cellulose and cellulose graft copolymers, indicating that the degradation mechanism is complex.

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