

Thermal Behavior of Cellulosic Graft Copolymers. II. Cotton Grafted with Binary Mixtures of Vinyl Acetate and Methyl Acrylate

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Synopsis

Thermal degradation of cotton, mercerized cotton, cotton grafted with vinyl acetate–methyl acrylate mixtures at different compositions, and mercerized cotton grafted with vinyl acetate–methyl acrylate mixture at a composition of 60:40 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 mercerization shows a little effect upon thermic properties of cotton cellulose, making cotton thermally more stable. Graft copolymerization of vinyl acetate–methyl acrylate mixture makes cotton thermally less stable if the composition of the copolymer grafted is 100, 90, and 70 mol % VA, while in the case of cellulose graft copolymers with compositions of VA–MA of 80:20, 20:80, 5:95, and 0:100 the thermal stability is higher than that of original cotton. The thermal stability of the mercerized cotton grafted with vinyl acetate–methyl acrylate mixture with a composition of 60:40 depends on the percent grafting yield. The thermal stability of mercerized cotton grafted with the monomer mixture is higher than that of cotton grafted with that monomer mixture. The degradation of cellulose and cellulose graft copolymers is complex as is shown by DTA thermograms and kinetic parameters.

INTRODUCTION

Chemical modification of cotton by way of graft copolymerization with various vinyl monomers has been studied very extensively.^{1–5} However, only limited information is available on the thermal behavior of grafted cottons.^{6–10} With respect to the thermal behavior of cotton grafted with binary mixtures of vinyl monomers, only Sharma et al.¹⁰ examined the thermal stability of cotton grafted with acrylamide–acrylonitrile mixture of different compositions.

In a previous work,¹¹ we reported the study of the thermal behavior of cotton grafted with vinyl acetate and methyl acrylate. In this communication we report our results on the thermal behavior of cotton grafted with binary mixtures of vinyl acetate–methyl acrylate of different compositions. This study has also been extended to mercerized cotton and mercerized cotton grafted with the binary mixture of vinyl acetate–methyl acrylate.

EXPERIMENTAL

Samples

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

Sample (i) purified cotton was the same as that described in Part I¹¹; sample (ii) mercerized cotton¹² and dried over phosphorous pentoxide; samples (iii–xi) cotton grafted with binary mixtures of vinyl acetate–methyl acrylate of different compositions [cellulose-*g*-P(VA-co-MA)] using ceric ion as initiator¹³; samples (xii–xiii) mercerized cotton grafted with the binary mixture of vinyl acetate–methyl acrylate [celluloseII-*g*-P(VA-co-MA)] at a composition of VA–MA 60 : 40 using ceric ion as initiator,¹³ and with a grafting yield of 153 and 219%, respectively.

Thermogravimetric and Differential Thermal Analyses

Thermogravimetric (TG), derivative thermogravimetric analyses (DTGA), and differential thermal analysis (DTA) were carried out as described previously in Part I.¹¹

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Figure 1 shows dynamic TGA and DTGA curves of purified cotton and mercerized cotton. Thermal decomposition of both cotton samples 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

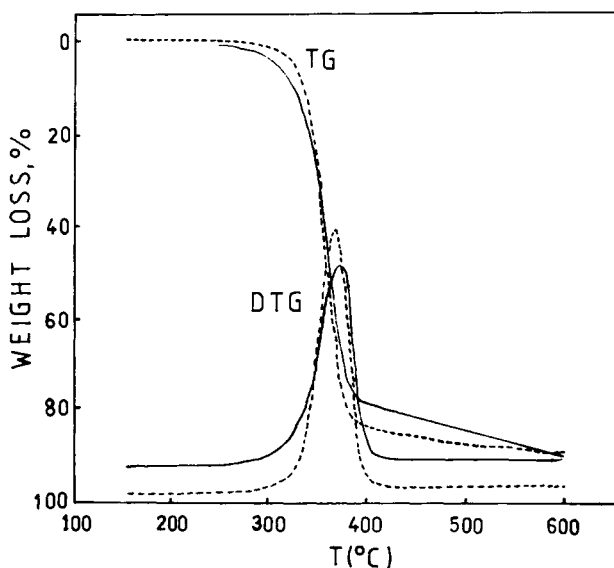


Fig. 1. TGA and DTGA curves of cotton: (—) purified (---) mercerized. Heating rate = 10°C/min.

TABLE I
Effect of Mercerization on the Thermal Decomposition of Cotton Cellulose

Sample	T_i (°C)	T_m (°C)	Residue (%)	Char (%)
Purified cotton	261	369	22.2	15.5
Mercerized cotton	266	362	19.4	13.4

place. During the second stage, temperatures $> 400^\circ\text{C}$, undecomposed cellulose and other impurities which amount to about 20% of the total weight are lost.

Table I shows 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 mercerized cotton begins at a higher temperature than that of purified cotton. However, the maximum rate of cellulose pyrolysis occurred at 362 and 369°C for mercerized cotton and purified cotton, respectively. The percent residue and percent char for mercerized cotton are lower than that for purified cotton.

Although the structure of native cellulose fibers remains fibrillar in nature after mercerization,¹⁴ other changes occur. The degree of disorder increases and the crystal structure is converted from cellulose I to cellulose II form. The cellulose II lattice is more densely packed than the cellulose I lattice and the cellulose molecules are more strongly interbonded. The slightly higher thermal stability on mercerized cotton may be explained taking into account the additional intermolecular bonding.

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. T_D values at 10 and 20% weight losses are higher for mercerized cotton, while those values beyond 30% weight loss are higher for purified cotton.

Figures 2 and 3 show dynamic TGA and DTGA curves of cellulose-*g*-P(VA-co-MA). As can be seen the pyrolysis of cellulose-*g*-P(VA-co-MA) samples take place in two or three steps from 150 to 550°C , depending on the composition of the grafted polymer P(VA-co-MA). Thus, the pyrolysis of the graft copolymer samples, cellulose-*g*-PVA, and cellulose-*g*-P(VA-co-MA) with an average

TABLE II
Temperature of Decomposition at Different Weight Losses
of Purified Cotton and Mercerized Cotton

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
Mercerized cotton	336	345	350	355	360	365	371	384

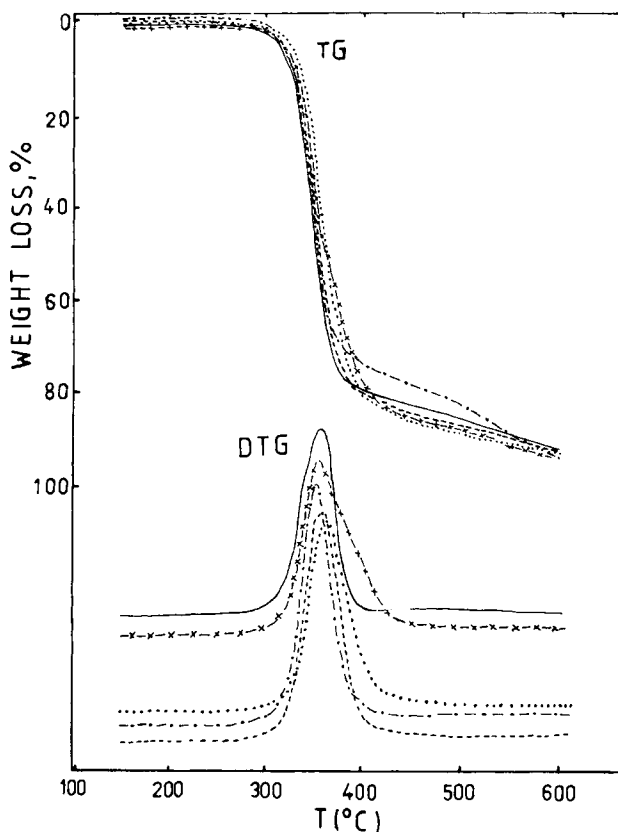


Fig. 2. TGA and DTGA curves of cotton grafted with poly(vinyl acetate-co-methyl acrylate) at different compositions: (—) VA-MA 100:0; (---) VA-MA 90:10; (···) VA-MA 80:20; (- × -) VA-MA 70:30; (- · - ·) VA-MA 50:50. Heating rate = 10°C/min.

composition of the grafted polymer of 90, 80, and 70 mol % VA, takes place in two steps. In the first stage, temperature range 260–390°C, most of the decomposition of cellulose graft copolymer samples takes place, and during the second stage, temperatures > 390°C, about 20–28% of the total weight of graft copolymer is lost.

On the other hand, as can be seen from the DTGA curve of the cellulose-*g*-P(VA-co-MA) sample with 50 mol % VA, the first step of thermal degradation, temperature range 260–450°C, shows a little tendency of separation in the other two processes. This tendency is evident in the thermograms of cellulose-*g*-P(VA-co-MA) samples with 40, 20, 5, and 0 mol % VA. In the case of the graft copolymer sample with 40 mol % VA, the two first processes (temperature range 270–418°C) are superposed and it is difficult to know exactly the percent of the total weight of the sample lost in each process. However, in the case of the samples with 20, 5, and 0 mol % VA, the two processes are only partially superposed and in the first step (temperature range 250–460°C) the 50, 33, and 22% of total sample weight are lost, respectively, while during the second step the 43, 67, and 75% of sample weight are lost.

Table III shows T_i and T_m , percent residues and percent char for cellulose-*g*-P(VA-co-MA) graft copolymers and ungrafted cellulose. Results of Table III

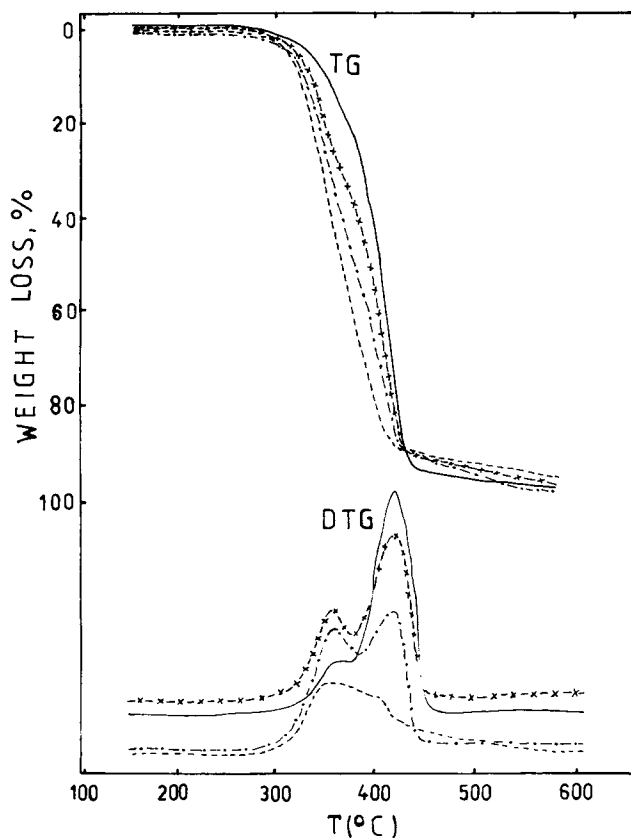


Fig. 3. TGA and DTGA curves of cotton grafted with poly(vinyl acetate-co-methyl acrylate) at different compositions: (---) VA-MA 40:60; (-·-·-) VA-MA 20:80; (-·-·-) VA-MA 5:95; (—) VA-MA 0:100. Heating rate = 10°C/min.

TABLE III
Thermal Analytical Data for Cotton Grafted with Vinyl Acetate-Methyl Acrylate Mixture at Different Compositions

Sample	VA (mol %)	MA (mol %)	Grafting yield (%)	T_i (°C)	T_{mI}^a (°C)	T_{mII}^b (°C)	Residue (%)	Char (%)
Purified cotton	—	—	—	261	369	—	22.2	15.5
Cotton grafted with VA-MA mixture	100	0	89	261	352	—	21	14
	90	10	127	276	350	—	22	13.5
	80	20	148	283	355	—	22.5	13
	70	30	168	268	345	—	28.2	15.7
	50	50	222	263	350	—	20.4	11.6
	40	60	202	271	348	—	12	5.2
	20	80	208	276	355	412	7.9	6.5
	5	95	195	250	353	414	9.1	6
	0	100	430	282	357	416	7.2	5.6

^a T_m value for the first step.

^b T_m value for the second step.

TABLE IV
 Temperature of Decomposition at Different Weight Losses of Cotton and Cotton Grafted with Vinyl Acetate-Methyl Acrylate Mixture of Different Compositions

Sample	VA	MA	Grafting	Temperature of decomposition (°C) at weight loss of						
				10	20	30	40	50	60	70
Purified cotton	—	—	—	326	342	351	357	363	369	377
Cotton grafted with VA-MA mixture	100	0	89	326	336	343	348	353	358	366
	90	10	127	324	335	341	347	353	360	369
	80	20	148	337	348	356	363	372	382	394
	70	30	168	324	333	338	344	350	359	376
	50	50	222	332	338	346	353	362	372	385
	40	60	202	324	336	345	356	366	376	388
	20	80	208	329	345	355	367	379	393	404
	5	95	195	339	350	366	383	395	403	411
	0	100	430	351	375	390	400	405	411	416

indicate that, in the case of monomer mixtures, the decomposition reaction begins at comparatively higher temperature than that of vinyl-acetate-grafted cotton, but at lower temperature than that of methyl-acrylate-grafted cotton. In general, the decomposition of cellulose grafted with binary mixtures of vinyl acetate-methyl acrylate starts at a higher temperature than that of ungrafted cotton. T_m values for the first step of pyrolysis are roughly similar for all copolymer samples, and lower than T_m values of ungrafted cotton. However, T_m values for the second step of pyrolysis of graft copolymers are higher than T_m value of ungrafted cotton.

The highest percent residue is observed for cellulose graft copolymers with a composition of the binary mixture VA-MA in the range 100-50 mol % VA and those values (28-20%) are similar to that of ungrafted cotton (22.2%). However, the percent residue for graft copolymers with a composition between 40 and 0 mol % VA is remarkably lower (2-7%).

The same trend as that observed in percent residue is observed in percent char.

Table IV shows the decomposition temperature (T_D) for cellulose-*g*-P(VA-co-MA) graft copolymers and ungrafted cellulose.

As can be seen, T_D values for graft copolymer samples with 100, 90, and 70 mol % VA are lower than those for ungrafted cotton, whereas T_D values for the graft copolymer sample with 40 mol % VA are lower than those for ungrafted cotton up to a conversion of 40%, beyond which temperature values for the former are higher than those for the latter. In the case of the graft copolymer with 50 mol % VA, although T_D value at 10% decomposition is higher than that of ungrafted cellulose, T_D values up to a conversion of 50% are lower than those of ungrafted cellulose and beyond that degree of conversion T_D values are higher for the graft copolymer. However, the graft copolymer samples with 80, 20, 5, and 0 mol % VA show T_D values higher than those for untreated cotton.

From these results it can be concluded that the effect of grafting of binary mixture of vinyl acetate-methyl acrylate onto cellulose on the thermal stability of cellulose depends on the composition of the grafted polymer P(VA-co-MA).

The cellulose graft copolymers with 100, 90, and 70 mol % VA have a lower thermal stability than that of ungrafted cellulose, while in the case of the graft copolymer sample with 40 mol % VA, although decomposition starts at comparatively lower temperatures as compared with cotton, grafting of binary mixture of VA-MA retards the decomposition of cellulose beyond 357°C. In the case of the graft copolymer with 50 mol % VA decomposition commences at comparatively higher temperatures as compared with cotton, but this is followed by rapid decomposition up to 362°C and beyond that temperature grafting of binary mixture of VA-MA results in a delay in the decomposition of cotton. The cellulose graft copolymer samples with 80, 20, 5, and 0 mol % VA have a higher thermal stability than that of ungrafted cotton.

Figure 4 shows dynamic TGA and DTGA curves of cellulose-II-*g*-P(VA-co-MA) graft copolymer samples having 153 and 219% grafting yield and with a composition of VA-MA of 60:40.

As can be seen, the pyrolysis of celluloseII-*g*-P(VA-co-MA) sample having 153% grafting yield takes place in two steps from 150 to 550°C. In the first

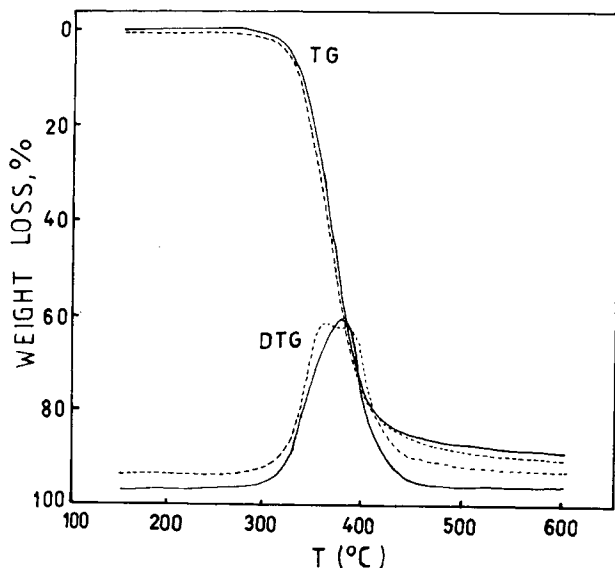


Fig. 4. TGA and DTGA curves of mercerized cotton grafted with poly(vinyl acetate-co-methyl acrylate) at a composition of VA-MA of 60:40: (—) 153% grafting yield; (---) 219% grafting yield. Heating rate = 10°C/min.

stage, temperature range 280–415°C, most of decomposition of cellulose graft copolymer takes place, and, during the second stage, temperatures > 415°C, about 20% of the total weight of the sample is lost. However, in the case of the graft copolymer sample with 219% grafting yield, the first step of thermal degradation shows a tendency of separation in two other processes (DTGA curve). The two first stages, temperature range 266–415°C, are superposed and about 85% of the total weight of the sample is lost, while in the third stage, temperatures > 415°C, about 15% of the total weight is lost.

Table V shows T_i and T_m , percent residue and percent char for celluloseII-*g*-P(VA-co-MA) graft copolymers and ungrafted mercerized cotton. Results of Table V indicate that, in the case of the graft copolymer having 153% grafting yield, the decomposition reaction begins at a higher temperature than that of ungrafted mercerized cotton, while, in the case of the graft copolymer sample with 219% grafting yield, the decomposition begins at the same temperature of that of ungrafted mercerized cotton.

TABLE V
Thermal Analytical Data for Mercerized Cotton Grafted
with Vinyl Acetate-Methyl Acrylate Mixture

Sample	VA (mol %)	MA (mol %)	Grafting yield (%)	T_i (°C)	T_{m1} (°C)	Residue (%)	Char (%)
Mercerized cotton	—	—	—	266	362	19.4	13.4
Mercerized cotton	60	20	153	274	376	20	13
grafted with VA-MA mixture	60	40	219	266	353	16	8.2

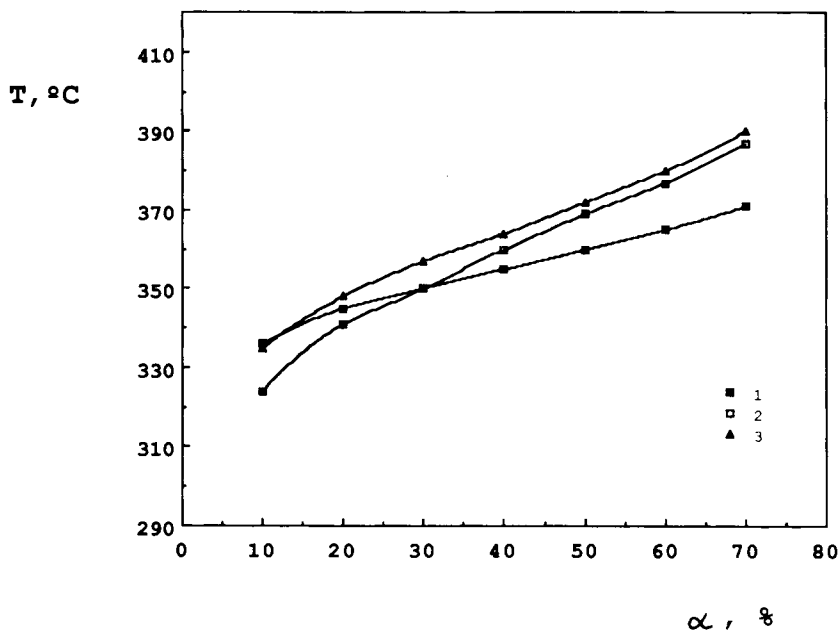


Fig. 5. Temperature dependence of the degree of conversion for mercerized cotton grafted with vinyl acetate-methyl acrylate mixture (VA:MA 60:40) comparatively with the initial mercerized cotton: (1) mercerized cotton; (2) grafted cotton 153% grafting yield; (3) grafted cotton 219% grafting yield.

T_m value for the first step of pyrolysis of the graft copolymer sample having 219% grafted yield is the same as that for the ungrafted mercerized cotton, while T_m value for the graft copolymer sample with 153% grafting yield is higher than that of both ungrafted mercerized cotton and graft copolymer sample with 219% grafting yield.

The percent residue for graft copolymer sample having 219% grafting yield are lower than those for the graft copolymer sample with 153% grafting yield. Percent residue and percent char for the latter are similar to that of ungrafted mercerized cellulose.

Figure 5 shows the temperature dependence of the degree of conversion for celluloseII-*g*-P(VA-co-MA) and ungrafted mercerized cotton.

The values of temperature beyond 10% decomposition for the graft copolymer sample having 153% grafting yield are higher than those for ungrafted mercerized cotton, while, in the case of the graft copolymer with 219% grafting yield, temperature values up to 30% conversion are lower than those of ungrafted cellulose, but beyond 40% conversion the temperature values are higher than those for ungrafted mercerized cotton.

From these results it can be deduced that the effect of grafting of binary mixture of vinyl acetate-methyl acrylate, at a composition of VA-MA of 40:60, onto mercerized cellulose on the thermal stability of mercerized cellulose depends on the percent grafting yield.

The cellulose graft copolymer having 153% grafting yield has a higher thermal stability than that of ungrafted mercerized cellulose. However, in the case of the graft copolymer having 219% grafting yield, although decomposi-

tion commences at comparatively lower temperatures as compared with mercerized cotton, grafting of binary mixture of vinyl acetate–methyl acrylate results in a delay in the decomposition of mercerized cotton beyond 355°C.

If temperature values at different degrees of conversion for celluloseII-*g*-P(VA-co-MA) graft copolymers with 153 and 219% grafting yield and with a composition of VA–MA of 60 : 40 are compared with those values for cellulose-*g*-P(VA-co-MA) graft copolymers with a composition of VA–MA of 50 : 50 and 70 : 30 and with percent grafting yield of 222 and 168%, respectively (Fig. 6), it is observed that temperature values for celluloseII-*g*-P(VA-co-MA) graft copolymer sample with a composition of VA–MA of 60 : 40 and 153% grafting yield are the highest, and those values for cellulose-*g*-P(VA-co-MA) sample with a composition of VA–MA of 70 : 30 and grafting yield of 168% are the lowest. However, in the case of celluloseII-*g*-P(VA-co-MA) sample with 219% grafting yield and a composition of VA–MA of 60 : 40 and cellulose-*g*-P(VA-co-MA) sample with a composition of VA–MA of 50 : 50 and 222% grafting yield, although decomposition of the former commences at comparatively lower temperatures, temperature values beyond 20% conversion are higher for the latter.

From this comparison it can be concluded that the thermal stability of celluloseII-*g*-P(VA-co-MA) samples with a composition of VA–MA of 60 : 40 is higher than that of cellulose-*g*-P(VA-co-MA) samples with a composition of VA–MA of 50 : 50 and 70 : 30.

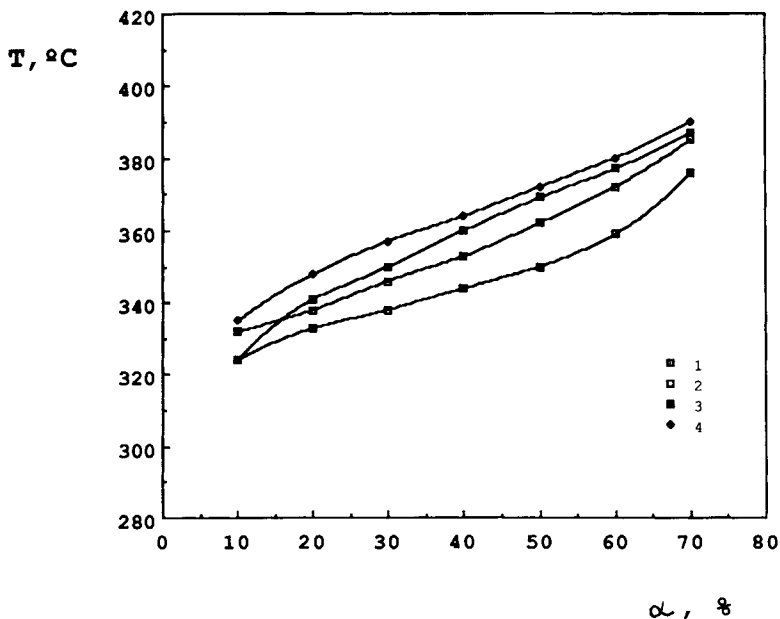


Fig. 6. Temperature dependence of the degree of conversion for cotton grafted with vinyl acetate–methyl acrylate mixture comparatively with mercerized cotton grafted with vinyl acetate–methyl acrylate mixture: (1) grafted cotton 70 mol % VA, 168% grafting yield; (2) grafted cotton 50 mol % VA, 222% grafting yield; (3) grafted mercerized cotton 60 mol % VA, 153% grafting yield; (4) grafted mercerized cotton 60 mol % VA, 219% grafting yield.

Calculation of Kinetic Parameters

As in the previous work,¹¹ the kinetic parameters were calculated from TG curves using the method of Friedman,¹⁵ Kissinger,¹⁶ Flynn and Wall,¹⁷ and Reich.¹⁸

Figure 7 shows the TGA and DTGA curves for cellulose-*g*-P(VA-co-MA) graft copolymer sample with a composition of VA-MA of 50:50 at different heating rates. Note that the curves are displaced to higher temperatures with increasing heating rate.

The values of E , n , and A determined applying the above-mentioned methods are given in Table VI for ungrafted cellulose samples (purified and mercerized cotton) and cellulose grafted copolymers [cellulose-*g*-P(VA-co-MA) and celluloseII-*g*-P(VA-co-MA)]. 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

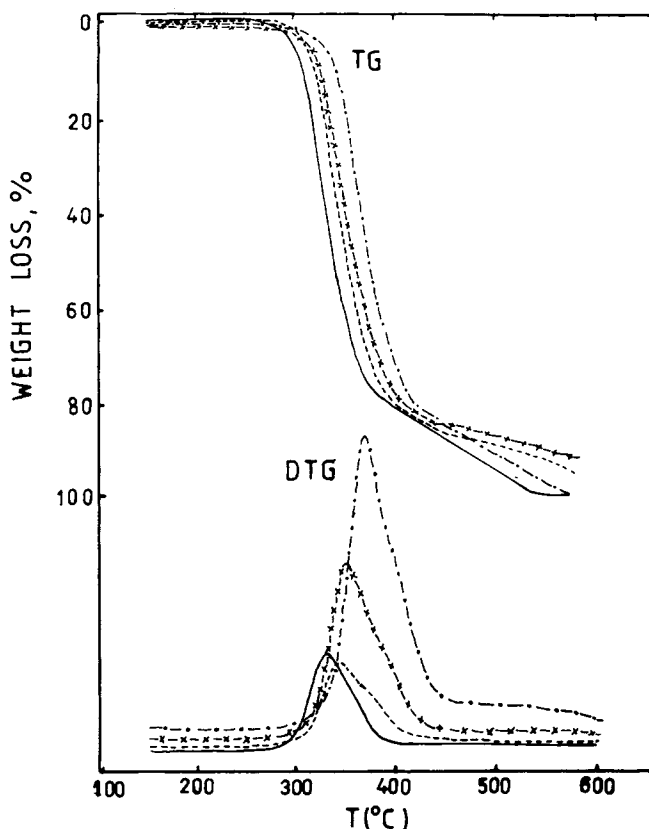


Fig. 7. TGA and DTGA curves for cotton grafted with vinyl acetate-methyl acrylate mixture at a composition of VA-MA of 50:50 at various heating rates: (—) 2°C/min; (---) 5°C/min; (-×-) 10°C/min; (···) 20°C/min.

TABLE VI
Kinetic Characteristics of the Thermal Degradation of Cellulose, Mercernized Cellulose, Cellulose Grafted with Vinyl Acetate-Methyl Acrylate Mixtures,
and Mercernized Cellulose Grafted with Vinyl Acetate-Methyl Acrylate Mixture

Sample	VA (mol %)	MA (mol %)	Grafting yield (%)	α (%)	E (kcal/mol)				Friedman		
					F ^a	K ^a	F-W ^a	R ^a	α (%)	n	A (min ⁻¹)
Purified cotton	—	—	—	10-70	47.1	30	40	39	10-45	0.3	5.3×10^{16}
Mercernized cotton	—	—	—	10-60	49.3	40	54	54.6	50-70	1	1.1×10^{17}
Cotton grafted with VA-MA mixture	100	0	89	30-60	46.7	42.3	44	44	35-60	1	4.7×10^{17}
	90	10	127	15-70	23.3	32.7	37 ^b	36.6 ^b	30-60	2.2	1.3×10^{17}
	80	20	148	10-70	30	34.5	39 ^b	38.5 ^b	20-45	0	5.7×10^9
	70	30	168	—	26.8 ^b	30.6	30 ^b	29.2 ^b	40-70	2.5	2.4×10^{10}
	50	50	222	30-80	36.5	36.4	34.9 ^b	34.8 ^b	30-70	1.6	1.5×10^{11}
	40	60	202	10-80	24.4	24.6	35.7 ^b	35.2 ^b	—	—	—
	20	80	208	5-35	28.6	23.4	31.9	32	10-30	0	1.1×10^{13}
	5	95	195	55-80	20.1 ^d	24.8	28.7	27.6	30-80	3	3.2×10^{13}
				10-30	20.3	24.8	25	25.8	—	10-80	1.3
	0	100	430	40-90	25	34.8	29.3	29.6	15-45	0.6	1.6×10^{10}
				10-60	27.2	26	28.3	27.2	—	—	—
Mercernized cotton	60	40	153	10-70	45	40.1	59.6	62.5	10-60	1.5	1.4×10^{16}
grafted with VA-MA mixture	60	40	219	10-60	41.5	32	53.7 ^b	53.9 ^b	10-60	1.9	9.6×10^{14}

^a F = Friedman's method; K = Kissinger's method; F-W = Flynn-Wall's method; R = Reich's method.

^b $E_{\alpha,0}$.

^c Degree conversion range 50-80%.

^d $E_{\alpha,0}$ of second step of pyrolysis.

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 VI indicate that two mechanisms of degradation are involved in the decomposition of cotton cellulose. The reaction mechanism for cellulose decomposition includes two processes.¹⁹⁻²¹ The first process consists in reduction of degree of polymerization by bond scission, appearance of free radicals, dehydration, formation of carbonyl and carboxyl groups, evolution of CO and CO₂, and production of a carbonaceous residue. The second one results in depolymerization of the molecule by cleavage of glycosyl units to form mainly levoglucosan, and this reaction is also accompanied by some decomposition of the original molecule as well as the anhydro sugar products.

The values of both activation energy and frequency factor obtained for both cotton samples are in agreement with those obtained by Bradbury et al.²² isothermally and Chatterjee and Conrad²³ using dynamic thermogravimetry. The activation energy values for purified cotton are lower than that of mercerized cotton. The reaction orders are similar for both cotton cellulose samples, while frequency factor value is higher for mercerized cotton.

From the results of Table VI it can be observed that the highest E value is obtained for cellulose-*g*-PVA sample. E values for the graft copolymer samples with compositions between 40:60 and 0:100 are lower than that of the samples with compositions between 90:10 and 50:50.

In the case of the copolymer samples having a composition between 90:10 and 40:60, the activation energy depends on the degree of conversion, indicating the complexity of the decomposition reaction. Table VII shows the influence of the transformation degree on the activation energy for the graft copolymer sample with 70 mol % VA. The activation energy values for the mixed monomer-grafted cotton samples lie between those obtained for the corresponding individual monomer-grafted samples (Table VI).

As for the graft copolymers celluloseII-*g*-P(VA-co-MA), the activation energy is slightly higher for the sample having 153% grafting yield, and the same trend is observed in frequency factor values, while reaction order is slightly higher for the sample with 219% grafting yield.

TABLE VII
Influence of the Transformation Degree on Activation Energy of Cotton Grafted with Vinyl Acetate-Methyl Acrylate Mixture at a Composition of VA-MA of 70:30

Sample	VA (mol %)	Grafting yield (%)	α (%)	Friedman		Flynn-Wall		Reich		
				E (kcal/mol)	$E_{\alpha,0}$	E	$E_{\alpha,0}$	E	$E_{\alpha,0}$	
Cotton grafted with VA-MA mixture	70	168	10	25.5	26.8	27.9	30	27.1	29.2	
			20	21.1		28		27		
			30	20.2		27		26.1		
			40	17.9			26.1		25	
			50	14.4			24.3		23.1	
			60	14.2			23.1		22	
			70	—			21.5		20.2	

Comparison of the cellulose grafted copolymer samples with ungrafted cellulose shows that the activation energy (Friedman's method) for cellulose grafted with vinyl acetate was roughly similar to that of purified cotton. However, activation energy for cellulose-*g*-P(VA-co-MA) samples was lower than that of ungrafted cotton. On the other hand, activation energy for celluloseII-*g*-P(VA-co-MA) sample with 219% grafting yield is slightly lower than that for mercerized cotton, while that value for the graft copolymer sample with 153% grafting yield is roughly similar to that of ungrafted mercerized cotton.

From the results shown in Table VI it can be deduced that two mechanisms are involved in the decomposition reaction of graft copolymer samples with 90, 50, and 5 mol % VA. However, in the case of graft copolymer samples celluloseII-*g*-P(VA-co-MA), only one mechanism of degradation is involved in the decomposition reaction of the sample.

The pyrolytic reaction of cellulose graft copolymers, cellulose-*g*-P(VA-co-MA), is complex since that of cellulose cannot be explained by a simple reaction,¹⁹⁻²¹ and that of VA-MA copolymers involves the three main processes of acetic loss, lactonization and chain scission.²⁴ These processes take place in an overlapping temperature range.

Differential Thermal Analysis

The DTA thermograms of (i) purified cotton, (ii) mercerized cotton, (iii-xi) cotton grafted with binary mixtures of vinyl acetate-methyl acrylate of different compositions, and (xii-xiii) mercerized cotton grafted with the binary mixture of vinyl acetate-methyl acrylate at a composition of 60:40 were recorded in the temperature range 50-460°C and are shown in Figures 8-11. The peak temperature for various endotherms is given in Table VIII.

As described in the previous work,¹¹ the DTA curve of purified cotton shows two endothermic peaks (Fig. 8) similar to that observed by other authors.^{25,26} A small endotherm in the temperature range 80-182°C, followed

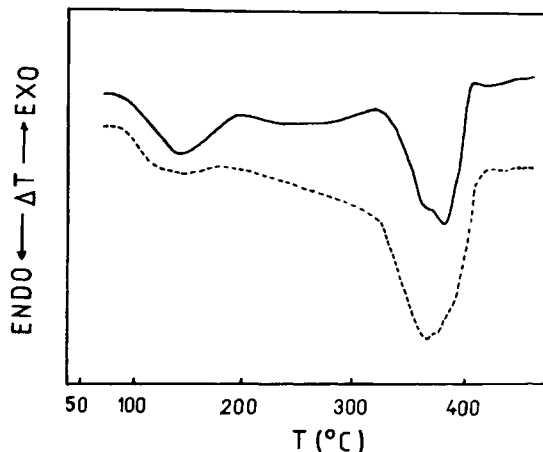


Fig. 8. DTA thermograms of ungrafted cotton: (—) purified cotton; (---) mercerized cotton. Heating rate = 20°C/min.

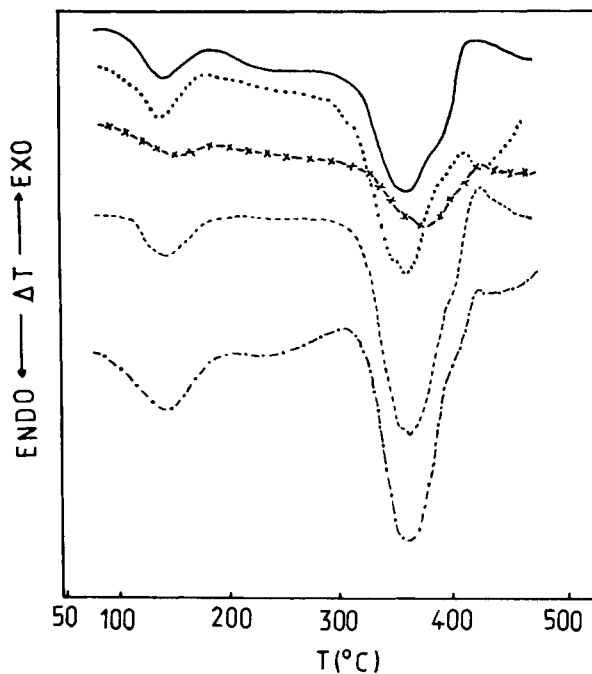


Fig. 9. DTA thermograms of cotton grafted with poly(vinyl acetate-co-methyl acrylate) at different compositions: (—) VA-MA 100:0; (···) VA-MA 90:10; (-x-) VA-MA 80:20; (- - -) VA-MA 70:30; (· · ·) VA-MA 50:50. Heating rate = 20°C/min.

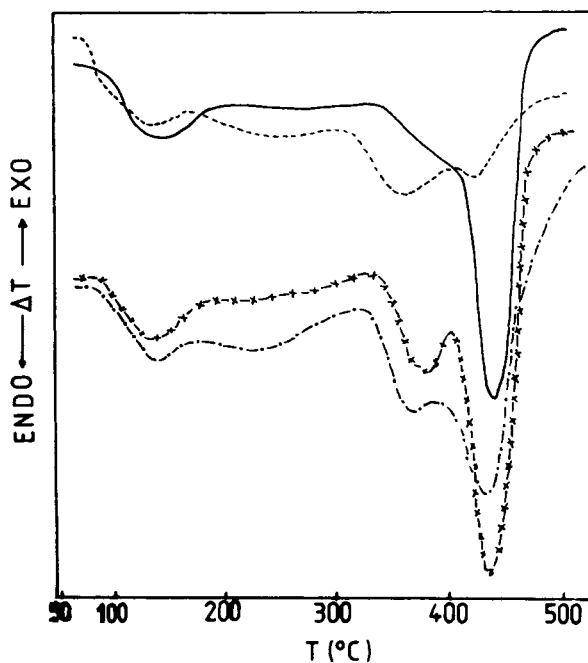


Fig. 10. DTA thermograms of cotton grafted with poly(vinyl acetate-co-methyl acrylate) at different compositions: (···) VA-MA 40:60; (-x-) VA-MA 20:80; (-x-) VA-MA 5:95; (—) VA-MA 0:100. Heating rate = 20°C/min.

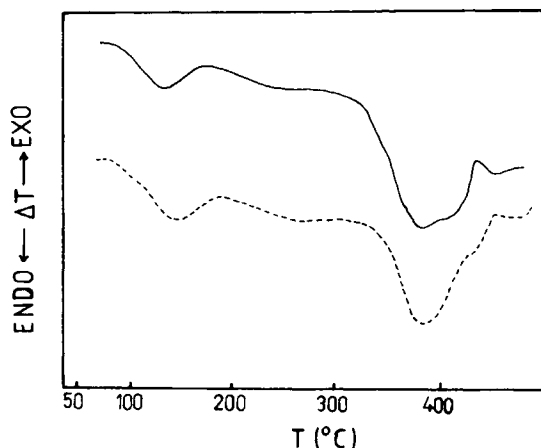


Fig. 11. DTA thermograms of mercerized cotton grafted with poly(vinyl acetate-co-methyl acrylate) at a composition of VA-MA of 60:40: (—) 153% grafting yield; (---) 219% grafting yield. Heating rate = 20°C/min.

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, although the DTA curve of mercerized cotton has the same shape as that of purified cotton, the peak minimum for the second endotherm takes place at a higher temperature, 367°C instead of 355°C. The first endotherm may be due to the evaporation of sorbed moisture and to a dehydration process involving the splitting off a hydroxy group and of a hydrogen between two hydroxyl groups to form water. The second one is due to the decomposition of the glycosyl units of cellulose by evolution of water, CO₂, and CO and formation of a charred residue, and to the cleavage of glycosyl units to form levoglucosan, other anhydrosugars, and low molecular weight sugar derivatives. The DTA curves of the graft copolymers cellulose-*g*-P(VA-co-MA), having different compositions of the grafted polymer, show two or three endotherms (Figs. 9 and 10).

The curves of the graft copolymer samples with compositions of VA-MA between 100:0 and 70:30 show two endotherms. The first one is in the temperature range 75–180°C, and the second one between 278 and 414°C. The peak minimum temperature is roughly similar for all samples. In the case of the samples having a composition of VA-MA of 90:10, 80:20, and 70:30, a shoulder is also observed at about 393°C; furthermore, the curve of the sample with the composition 80:20 shows a hump at about 344°C. These shoulders are not present either in DTA curve of ungrafted cellulose or in that of cellulose-*g*-PVA.

However, the DTA curves of the graft copolymer samples with compositions of VA-MA between 50:50 and 0:100 show three endotherms, the second one and the third one being superposed. The first endotherm is in the temperature range 80–190°C, the peak minimum temperature of the second endotherm is between 360 and 370°C, the curve of the sample with the composition 50:50 also shows a shoulder at about 390°C, and the peak minimum temperature of the third endotherm is in the temperature range

TABLE VIII
Peak Temperature in the DTA Thermograms for Cellulose, Mercerized Cellulose and Mercerized Cellulose Grafted with Binary Mixtures of Vinyl Acetate and Methyl Acrylate

Sample	VA (mol %)	MA (mol %)	Grafting yield (%)	Endotherm I		Endotherm II		Endotherm III		
				Temp range (°C)	T_i	T_m (°C)	T_f	T_i	T_m (°C)	T_f
Purified cotton	—	—	—	80-182	317	355 ^a 374 ^a	395	—	—	—
mercerized cotton	—	—	—	80-185	314	367 ^a	395	—	—	—
VA-MA grafted cotton	100	0	89	80-180	295	353	402	—	—	—
	90	10	127	80-170	300	355 391 ^b	414	—	—	—
	80	20	148	80-170	278	365 344 ^b 393 ^b	412	—	—	—
	70	30	168	75-175	300	355 395 ^b	412	—	—	—
	50	50	222	80-170	296	360	—	—	426	—
	40	60	202	80-170	312	365	—	—	424	—
	20	10	208	80-170	316	360	—	—	423	—
	5	95	195	80-180	328	371	—	—	431	462
	0	100	430	80-190	329	—	—	—	433	464
VA-MA grafted mercerized cotton	60	40	153	80-190	302	360 381 ^b	—	—	431	—
	60	40	219	80-190	309	355 398 ^b	419	—	450	—

^a Endotherm split into two peaks.

^b Shoulder.

423–433°C. The third endotherm is smaller than the second one in the case of the samples with a composition of VA–MA of 50 : 50 and 40 : 60, while in the case of the samples with a composition of VA–MA of 20 : 80, 5 : 95, and 0 : 100, the third one is the largest.

The DTA thermograms of celluloseII-*g*-P(VA-co-MA) graft copolymers with a composition of VA–MA of 60 : 40 and with a grafting yield of 153 and 219% show three distinct endotherms (Fig. 11). The second one is in the range 300–420°C, with its peak minimum at 360 and 355°C, respectively, and with a shoulder at about 391 and 398°C, respectively.

From the above results it can be concluded that two mechanisms are involved in the pyrolysis of both purified cellulose and mercerized cellulose in the temperature range 310–395°C. The same conclusion was deduced from the kinetic data (Table VI).

The second endotherm (Figs. 9 and 10) in the case of the graft copolymer samples with a composition of VA–MA between 90 : 10 and 50 : 50 indicates that there probably is a change of some kind in the mechanism of the process at about 390°C. The same conclusion can be deduced from the second endotherm (Fig. 11) of the DTA curves of the graft copolymer samples celluloseII-*g*-P(VA-co-MA).

CONCLUSIONS

Thermogravimetric analysis of purified cotton and mercerized cotton under nitrogen shows that the mercerization has a slight effect on the course of thermal degradation of cellulose, being the thermal stability of mercerized cotton lower than that of purified cotton.

It results from our study that the thermostability of vinyl acetate–methyl acrylate grafted cellulose is lower than that of initial cellulose if the composition of the grafted polymer is 100, 90, and 70 mol % VA, whereas the graft copolymers with compositions of 80, 20, 5, and 0 mol % VA have a higher thermal stability than that of ungrafted cellulose. However, in the case of the cellulose graft copolymers with compositions of VA–MA of 50 : 50 and 40 : 60, grafting of binary mixture of vinyl acetate and methyl acrylate results in a delay in the decomposition of cellulose beyond 360°C.

The effect of grafting of binary mixture of VA–MA at a composition of 60 : 40 onto mercerized cellulose is to make it more thermally stable if the grafting yield is 153%, whereas if the grafting yield is 219% the grafting of the monomer mixture results in a delay in the decomposition of mercerized cotton beyond 355°C. The thermal stability of cotton grafted with the binary mixture of vinyl acetate and methyl acrylate is lower than that of mercerized cotton grafted with that monomer mixture.

The DTA studies in nitrogen atmosphere indicated that the thermal degradation of cotton cellulose (purified and mercerized cotton) takes place via two endothermic processes. In the case of vinyl acetate–methyl acrylate grafted cotton with compositions between 100 and 70 mol % VA, the pyrolysis reaction takes place via two endothermic processes, while, in the case of graft copolymers with compositions of VA–MA between 50 : 50 and 0 : 100, the decomposition takes place via three endotherms, indicating that the decomposition reaction of graft copolymers is quite complicated. DTA of vinyl ac-

etate-methyl acrylate grafted mercerized cotton showed that the decomposition took place via three endothermic processes.

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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