Vinylic Graft Copolymers of Cellulose. II. Thermal Degradation of Cellulose and Its Vinylic Copolymers and Blends by Differential Scanning Calorimetry

C. FLAQUÉ* and S. MONTSERRAT

Laboratorio de Termodinámica y Fisicoquímica, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Cataluña, Colón 11, E-08222 Terrassa, Spain

SYNOPSIS

Cotton cellulose with different % NaOH treatments (mercerized), graft copolymers of cellulose prepared with vinyl acetate (VA) and methyl acrylate (MA) and Ce(IV) ions as initiator, and some blends of cellulose–copolymer PVA–PMA were submitted to differential scanning calorimetry (DSC) analysis in nitrogen atmosphere. Two aspects were considered: (a) moisture loss of celluloses with different % NaOH treatments, which showed differences attributed to structural changes in the amorphous region of cellulose-I and cellulose-II; (b) thermal degradation analysis of celluloses, their copolymers, and their blends. Experimental results show that thermal stability of celluloses decreases when % NaOH in mercerization increases. For cellulosic vinylic copolymers, the thermal stability increases with the grafting frequency (GF). The blends of cellulose–copolymer PVA–PMA were found to have lower thermal stability than the cellulosic copolymers and the cellulose alone, which was attributed to the acetic acid eliminated in the thermal decomposition of PVA–PMA. The present results seem to be in agreement with the thermal degradation mechanism of cellulose proposed by Patel et al. and provide useful confirmation that the free OH group content is a very important factor in the thermal stability of cellulose.

INTRODUCTION

Polymer degradation can be produced by many factors: temperature, water, oxygen, radiation, or biological organisms. The main chain and/or the side chains may be affected by the degradation process, and, consequently, irreversible losses in the physical properties of the material occur.

Many methods have been used to transform polymers and directly modified their properties. For cellulose this is possible by modification of the hydroxilyc groups of the monomer unit. In the present work, cellulose modification was performed by vinylic graft copolymerization, as described in a previous paper.[1]

The specific behavior of cellulosic copolymers is determined in terms of the extent of the substitution because the hydroxilyc groups have been blocked by the grafted vinylic chains.

It is very important to know whether the thermal behavior of cellulose derivatives is or is not affected by the chemical modification. For this reason, in the present work we have studied the thermal degradation of different vinylic grafted copolymers of cellulose, comparing it with the thermal degradation of the initial cellulose. These had been treated with NaOH (mercerized) in different concentrations and consequently had different crystallinity indices (CI). As we described in a previous paper,[1] to measure crystallinity of these cellulosic materials, the infrared ratio of absorbances proposed by Nelson and O'Connor was used as the crystallinity index (CI),[2] at 1372 cm^{-1} (C—H bending), which is the most suitable for detecting the crystallinity and should not be affected by differences in the amount of water absorbed on cellulose, and 2900 cm^{-1} (C—H stretching), which acts as the internal standard:

$$a_{1372 \text{ cm}^{-1}} / a_{2900 \text{ cm}^{-1}} \qquad (1)$$

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* To whom correspondence should be addressed.

The advantage of this ratio over others which have been used is that it can be applied to both celluloses I and II, and therefore to samples containing a mixed lattice. The thermal behavior of cellulose is affected by this treatment, as is shown in the results. We also considered the thermal degradation of some blends of cellulose with copolymers PVA–PMA as similar as possible to cellulosic copolymers, which showed different behavior.

Differential scanning calorimetry (DSC) is a useful technique for studying the thermal degradation of polymers, as well as some other thermal properties.

EXPERIMENTAL

Materials

The following samples of cellulose and its derivatives were selected for the present work.

(1) Cotton cellulose purified as previously described[1]: Cel. A.

(2) Cotton cellulose purified and treated with NaOH of different concentrations (mercerized cotton), for 24 h at room temperature:

> Cel. B: 10% NaOH
> Cel. C: 15% NaOH
> Cel. D: 20% NaOH

(3) Vinylic grafted copolymers of cellulose, prepared by grafting polymerization of VA and MA on cotton cellulose initiated by the Ce(IV) ion system.[1] Different cellulosic substrates (Cel. A, Cel. B, Cel. C, or Cel. D) and different volumetric ratios of monomers, V_{VA}/V_{MA} (80/20 = series 1; 85/15 = series 2; 90/10 = series 3; 95/5 = series 4, and 100/0 = series 5) were used to prepare cellulosic copolymers with different percentages of graft, %G, different numbers of polymeric side chains per cellulose unit, grafting frequencies, GF, and different viscosimetric average molecular weights M_v, and, thus, with different lengths of polymeric chains as described in Ref. 1.

(4) Copolymers of poly(vinyl acetate)–poly(methyl acrylate) without cellulose, prepared as above. The volumetric ratio V_{aq}/V_{mon} was 70/30 and the monomeric mixtures, $V_{VA}/V_{MA} = 80/20$ (copolymer CV1) and 90/10 (copolymer CV3).

(5) Blends of cellulose (Cel. C) and copolymers CV1 and CV3 of a similar weight percentage to %G of cellulosic copolymers:

> Cel. C + CV1: 189%
> Cel. C + CV1: 170%
> Cel. C + CV3: 31%

Blends were prepared by immersing the desired weight of cellulose in an acetone solution of poly(vinyl acetate)–poly(methyl acrylate) copolymer. The polymer percentage of each sample was calculated from the weight increase of the initial cellulose sample weight.

Before thermal analysis, samples were conditioned as follows: Cellulose, its vinylic copolymers, and its blends were pressed to achieve better uniformity, and therefore to prevent heat transfer problems in the material.

Samples of PVA, PMA and copolymers PVA–PMA were obtained in films cast from acetone solutions. All the samples were dried at 40°C in vacuum for 24 h.

Thermal Analysis

Thermal analysis was carried out by a Mettler thermoanalyzer TA 3000 with a differential scanning calorimetry cellule DSC 30, previously calibrated with indium, lead, and zinc standards. The heating rate was 10°C/min under nitrogen atmosphere.

About 10 mg of sample sealed in an aluminium cell were taken in each experiment. Scannings were carried out in two steps: The first step, from 0 to 200°C, was to eliminate the moisture absorbed by the sample. The loss of weight was determined before the second scanning between −40 and 450°C (500°C for homopolymers PVA, PMA, and copolymers PVA–PMA).

The initial temperature of the process, T_i, the final process temperature, T_f, the temperature at which the rate of process reaches its maximum value, T_{max}, the specific height of peak (or peaks), and the process enthalpy per gram of sample, ΔH, are shown in the present work. The process enthalpy has been calculated as the area peak or peaks between T_i and T_f (Fig. 1), and thus represents the total process enthalpy. Although T_i, T_f and T_{max} values vary with the rate of heating, in the present work it was the same for all the samples and these values may therefore reflect some differences in the process considered.

TEMPERATURE °C   HEAT FLOW
                                      EXOTHERMAL - - →
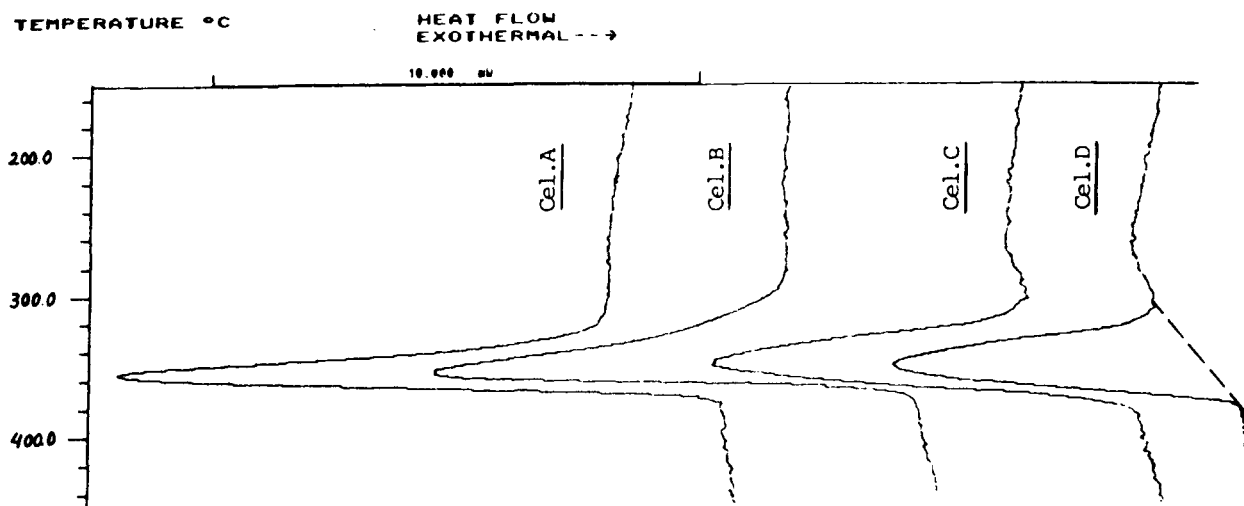
Figure 1   DSC thermograms of the degradation of different cellulose samples. In Cel. D, the base line for the area peak evaluation is shown.

RESULTS AND DISCUSSION

Cellulose Moisture

Four different cellulose samples (Cel. A, Cel. B, Cel. C, and Cel. D) were studied by DSC thermal analysis between 0 and 200°C. An endothermic peak, attributed to loss of moisture retained by the sample, was observed in this region.

The values of the initial and final temperature of the peak (T_i, T_f), the temperature range (ΔT) and the enthalpy of loss moisture (ΔH) referring to absorbed water are shown in Table I. The weight loss of the samples was about 5–8%.

Unmercerized cellulose (Cel. A) shows different behavior from mercerized ones (Cel. B, Cel. C, and Cel. D):

—The enthalpy of the loss moisture (ΔH) shows no relationship with that of the mercerized samples.

—The temperature range (ΔT) in which the loss moisture occurs is shorter than in the mercerized samples.

These facts are thought to be caused by some of the structural differences between the amorphous region of cellulose-I and cellulose-II.[3]

The following relationships between mercerized samples can be established:

—T_i and ΔH increases when the %NaOH in the mercerized treatment decreases and when the crystallinity index increases.

—ΔT increases with %NaOH in the mercerized treatment and when crystallinity index decreases.

The differences observed between the different cellulosic materials were attributed to their morphology, which implies different hygroscopic characteristics: Absorbed moisture in cellulose takes

Table I   Thermal Analysis Data of Moisture Loss Peak of Unmercerized and Mercerized Celluloses

	% NaOH in Merc.	IC	T_i (°C)	T_f (°C)	ΔT	ΔH (J/g Water)
Cel. A	—	0.68	30	150	120	1400
Cel. B	10	0.58	30	160	130	2940
Cel. C	15	0.53	25	160	135	2630
Cel. D	20	0.49	20	160	140	1160

Table II Data of the Main Peak of Thermal Degradation of Unmercerized and Mercerized Celluloses

	T_i (°C)	T_f (°C)	ΔT	T_{max} (°C)	ΔH (J/g)	h_s (mW/g)
Cel. A	315	375	60	355	210	1254.7
Cel. B	305	375	70	350	195	834.0
Cel. C	305	375	70	350	180	738.4
Cel. D	305	380	75	350	140	591.6

place, as is known, in the amorphous region, and its quantity is directly related to the number of free hydroxylic groups.[4-7]

Thermal Degradation of Cellulose

DSC thermograms of cellulose (Fig. 1) show two endothermic peaks attributed to thermal degradation of dry cellulose: the first one becomes apparent as a shoulder and begins at about 240°C (but only in mercerized samples Cel. C and Cel. D), and the second one from 300 to about 380°C.

These two peaks may indicate that the thermal degradation mechanism of cellulose takes place in two steps, as proposed by Patel et al.[8]: The first step, below 300°C, is ascribed to some chain scissions and, perhaps, to water molecules loss coming from the —OH primary groups. This step must be more important in more amorphous celluloses. The second step of degradation is much higher and may be due to the complete loss of —OH groups of the monomer units of cellulose and the breakdown of the pyranosic rings.

Data on T_i, T_f, ΔT, T_{max}, ΔH, and specific height h_s (in mW/g) of the main degradation peak of dry cellulose are shown in Table II.

It can be observed in the Table II that the unmercerized cellulose (Cel. A) has a T_{max} value higher

than mercerized ones, but there is no difference between them (Cel. B, Cel. C, and Cel. D). T_i values show the same fact. It is also observed that the temperature range of degradation (ΔT) tends to increase when %NaOH in mercerization increases, and the values of ΔH and h_s decrease when %NaOH increases.

According to these results, the thermal stability of cellulose decreases when %NaOH in mercerization increases, and thus when the free OH groups content increases.

Thermal Degradation of Homopolymers, PVA and PMA, and Copolymers of PVA–PMA

The DSC thermograms only show one peak for PMA, which is in agreement with the radical decomposition mechanism proposed for this material,[9] and two degradation peaks for PVA in agreement with the mechanism proposed by McNeil et al.,[10] which consists of two steps: The first one must be due to the acetic acid elimination and the second one must correspond to carbonization.

Copolymers of PVA–PMA, CV1, and CV3 show two peaks in their DSC thermograms. The first one, about 350°C, can be attributed to the first peak of PVA, and the second one, about 400°C, may be due to the overlap of the PMA degradation peak and the

Table III Data on Thermal Degradation of PVA, PMA, and Copolymers PVA–PMA: CV1 and CV3[a]

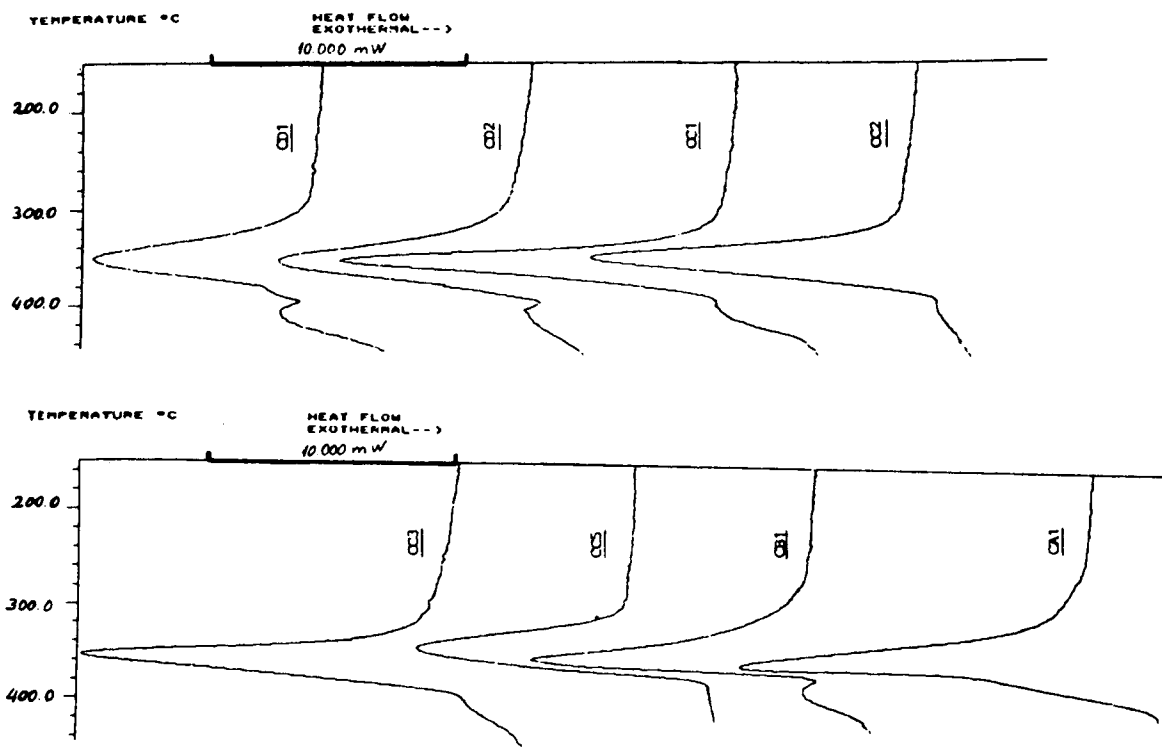|	T_i (°C)	T_f (°C)	ΔT	T_{max} (°C)	h_s (mW/g)	ΔH (J/g)
CV1	270	460	190	350.8	605.9	
				400.0	598.0	368.83
CV3	220	450	230	350.0	602.2	
				395.0	461.7	414.83
PAV	260	410	150	322.4	528.8	
	420	500	80	460.0	174.2	
PAM	290	430	140	390.0	2654.6	

[a] The weight loss was about 90% in all cases.

Figure 2 DSC thermograms of the degradation of vinylic copolymers of cellulose.

second degradation peak of PVA. Results of the thermal degradation of PVA and PMA and copolymers PVA–PMA (CV1 and CV3) are shown in Table III.

Thermal Degradation of Vinylic Copolymers of Cellulose

In the DSC thermograms of the degradation of vinylic copolymers of cellulose (Fig. 2) the following facts can be observed:

—For higher %G copolymers, two degradation peaks were observed: CD1, CD2, CB1, and CC1, whereas in the other cases only one was observed.

—The main degradation peak begins at about 290°C, so that it represents both the degradation process cellulose and the grafted vinylic chain.

—The first endothermic peak (beginning at about 240°C) of the most amorphous celluloses can not be observed in any case.

Table IV shows the experimental data on thermal degradation of vinylic copolymers of cellulose. In

order to make a comparative study of the thermal degradation behavior, the following series were selected:

Series 1: Graft copolymers of cellulose (from CA1 to CD1) prepared with different cellulosic substrates (Cel. A, Cel. B, Cel. C, and Cel. D) and with the same ratio $V_{VA}/V_{MA} = 80/20$.

Series C: Graft copolymers of cellulose (from CC1 to CC5) prepared with the same cellulosic substrate (Cel. C) and different V_{VA}/V_{MA} ratios: 80/20, 85/15, 90/10, 95/5, and 100/0, designated here as series 1, 2, 3, 4, and 5, respectively.

Figures 3 and 4 show the relationship between ΔH and T_{max} versus %G of copolymer for series 1 and C. Although Figure 3 (series 1) shows that ΔH and T_{max} decrease when %G increases, in Figure 4 (series C) ΔH and T_{max} increase with the %G. According to the results of a previous paper,[1] the grafting frequency, GF, decreases as in the following sequences:

—Series 1: CA1 > CB1 > CC1 > CD1.
—Series C: CC1 > CC2 > CC3 > CC4 > CC5.

Table IV Data on Thermal Degradation of Vinylic Copolymers of Cellulose[a]

	% G	T_i (°C)	T_f (°C)	T_{max} (°C)	ΔH (J/g)
CD1	305	290	450	351 406	316.62
CD2	184	280	450	355.8 403	332.85
CC1	170	290	450	358.6 397	378.70
CB1	136	280	450	363 400	380.07
CA1	63	280	450	377	513.67
CC2	53	290	450	356	362.00
CC3	33	290	450	352	329.36
CC5	9	290	380	337.9	298.94
(Cel. C	—	305	375	350	179.00)

[a] Weight loss was about 80–90%.

Therefore, it can be deduced that, in the thermal degradation process, ΔH and T_{max} values increase with the GF and therefore that the thermal stability increases with the number of $-OH$ groups of cellulose blocked by the grafting. This fact is similar to that observed in celluloses: ΔH of degradation increases when %NaOH in mercerization decreases, which is related to the number of free $-OH$ groups.

Thermal Degradation of Cellulose–Vinylic Polymer Blends

The following facts can be observed in the DSC thermal degradation curves of some blends of cellulose (Cel. C) and copolymers PVA–PMA in a similar weight percentage as the cellulosic grafted copolymers:

—The main degradation peak appears in the same region as the cellulose degradation main peak and the first one of the vinylic copolymer (about 350°C).

—The second peak, less important, appears near the region of the second degradation peak of copolymer PVA–PMA (about 400°C). In the case of cellulosic copolymers, this peak was only as a shoulder.

Figures 5 and 6 show the DSC thermal degradation curves for the vinylic copolymer of cellulose,
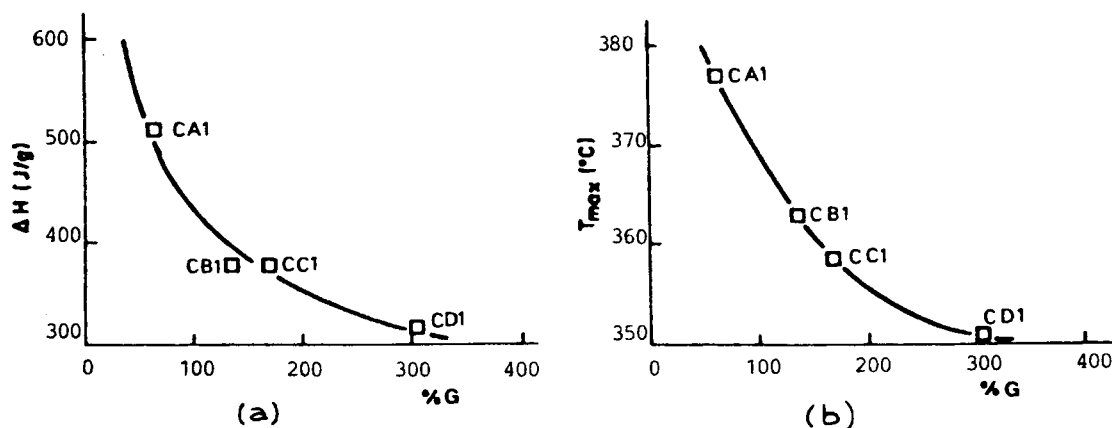
Figure 3 (a) Degradation enthalpy and (b) temperature of degradation peak maximum of vinylic copolymers of cellulose vs % grafting, for series 1 (same ratio $V_{VA}/V_{MA} = 80/20$) and different cellulosic substrates (Cel. A, Cel. B, Cel. C, and Cel. D).
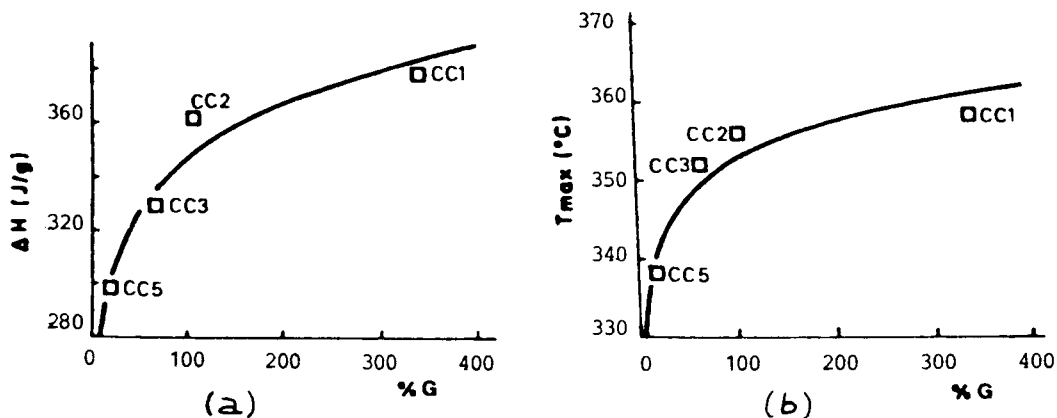
Figure 4   (a) Degradation enthalpy and (b) temperature of degradation peak maximum of vinylic copolymers of cellulose vs. % grafting, for series C (same cellulosic substrate, Cel. C, and different ratio V_{VA}/V_{MA}).

blends of cellulose and copolymers PVA–PMA, whose composition may be similar to that of the vinylic chain grafted onto cellulose. The weight percentage of vinylic copolymer in the blends with cellulose is also similar to that of the grafted cellulosic copolymer. These figures also show the thermal degradation curves of cellulose and copolymers PVA–PMA alone. Results on thermal degradation of cellulose and copolymer PAV–PMA blends are shown in Table V.

To study some of the differences observed between blends and copolymers, it has been assumed
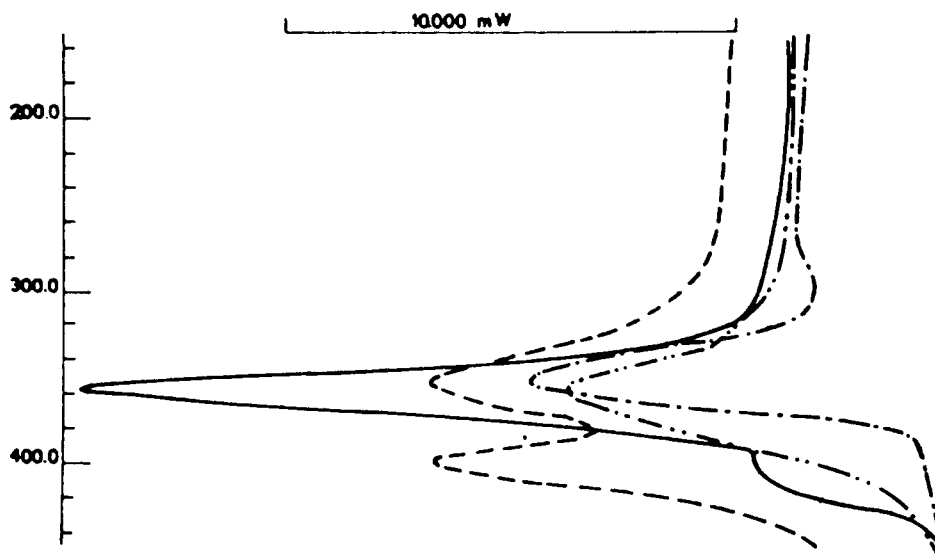
that the degradation enthalpy of blends could be calculated as a sum of ΔH_c of cellulose and ΔH_p of copolymer PVA–PMA using the relation

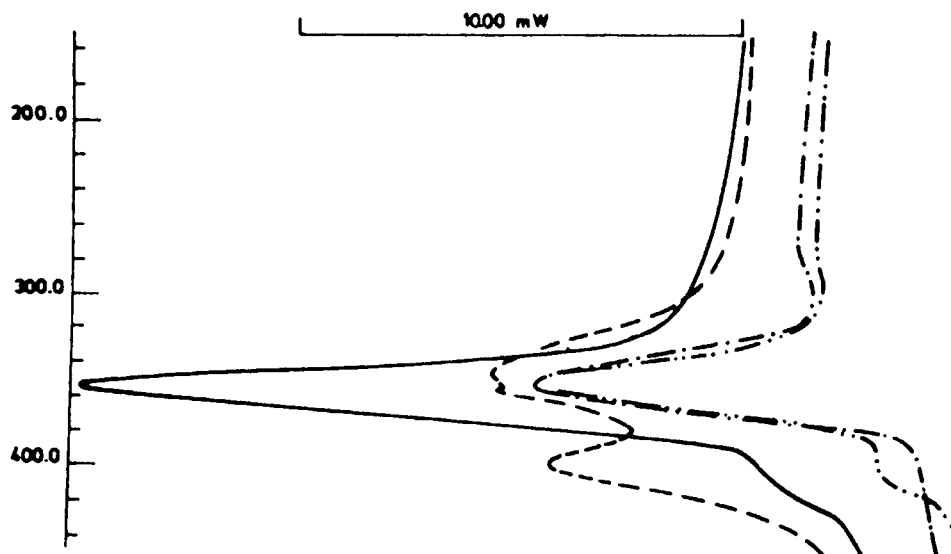$$\Delta H_{th} = m_c \, \Delta H_c + m_p \, \Delta H_p \qquad (2)$$

where

m_c = cellulose mass in 1 g of sample

m_p = polymer mass in 1 g of sample

Figure 5   DSC thermograms of degradation for vinylic copolymer of cellulose, CC1 170%G (– – –), blend of cellulose, Cel. C, and copolymer PVA–PMA 170% weight (– · · –), cellulose, Cel. C (– · –), and copolymer PVA-PMA, whose composition may be similar to that of the vinylic chain grafted onto cellulose (– – –).

Figure 6 Thermal degradation curves for vinylic copolymer of cellulose, CC3 33%G (– – –), blend of cellulose, Cel. C, and copolymer PVA–PMA 33% in weight (– · · –), cellulose, Cel. C (– · –), and copolymer PVA–PMA, whose composition may be similar to that of the vinylic chain grafted onto cellulose (– – –).

ΔH_c = degradation enthalpy of cellulose (in J/g)

ΔH_p = degradation enthalpy of polymer (in J/g)

In all the samples considered ΔH_{th} was higher than ΔH_{exp}, as Table VI shows. According to Table VI, thermal degradation of cellulose with copolymers PVA–PMA seems to cause an effect which makes the process easier: probably due to the acetic acid coming from PVA decomposition which can act as a catalyzer in the intramolecular dehydratations of cellulose.

On the other hand, the degradation enthalpy and the specific height of the main degradation peak of grafted copolymers are always higher than those of the corresponding blends (CC1 and Cel. C + CV1; CC3 and Cel. C + CV3), which may be indicative

of a higher thermal stability of the grafted cellulosic copolymers than the similar % weight blends.

The observations reported in Table VI provide useful confirmation that the free –OH groups content is an important factor in the thermal stability of cellulose.

The results found in this paper seem to confirm the thermal degradation mechanism proposed by Patel et al.[8] for cellulose and cellulose acetates: For cellulosic grafted copolymers some of the intramolecular dehydrations are not possible because their –OH groups are substituted by grafting, and removal of other products (more difficult to eliminate) may occur instead of the water elimination. Therefore, the thermal stability increases. For blends, intramolecular dehydrations of the cellulose backbone are catalyzed by the acetic acid of PVA–PMA decomposition, and their thermal stability is lower.

Table V Data on Thermal Degradation of Some Blends of Cellulose (Treated with 15% NaOH, Cel. C) and Copolymers PVA–PMA

	% V[a]	T_i (°C)	T_f (°C)	T_{max} (°C)	h_s (mW/g)	ΔH (J/g)
Cel. C + CV1	189	280	450	354.3	544.5	249.18
Cel. C + CV1	170	280	450	354.4	497.9	240.04
Cel. C + CV3	31	300	420	350.0	752.1	206.00
				400.0		

[a] % V = weight percentage of vinylic copolymer in the blend.

Table VI Degradation Enthalpy of Cellulose–Copolymer PVA–PMA Blends, Theoretically Calculated as the Relation (1) ΔH_{th} and Experimentally Obtained ΔH_{exp}

	% V[a]	m_c	m_p	ΔH_{th} (J/g)	ΔH_{exp} (J/g)
Cel. C + CV1	189	0.35	0.65	303.4	249.2
Cel. C + CV1	170	0.37	0.63	295.2	240.0
Cel. C + CV3	31	0.76	0.24	235.3	206.0

[a] % V = weight percentage of vinylic copolymer in the blend.

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