Thermal Degradation of Celluloses and Their Vinylic Copolymers by Thermogravimetric Analysis

C. FLAQUÉ,[1] S. MONTSERRAT[2]

[1] Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyers Industrials,
Universitat Politècnica de Catalunya, Colón 11, E-08222 Terrassa, Spain

[2] Departament de Màquines i Motors Tèrmics, Escola Tècnica Superior d'Enginyers Industrials,
Universitat Politècnica de Catalunya, Colón 11, E-08222 Terrassa, Spain

ABSTRACT: Thermal degradation of unmercerized and mercerized cotton cellulose with different % NaOH solutions and grafted vinylic copolymers with different mixtures of vinyl acetate-methylacrylate[1] have been studied by thermogravimetric analysis (TGA) in nitrogen between 25 and 600°C at different heating rates. The differences between unmercerized and mercerized samples are related to structural differences between cellulose-I (native) and cellulose-II. The grafted cellulosic vinylic copolymers have shown that their thermal stability depends upon the cellulosic substrate and the grafting percentage. From our results, it can be deduced that it is possible to prepare the cellulosic materials with good thermal stability, short degradation temperature interval, and various residues at the end of degradation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 201–209, 1999

Key words: cellulose; vinylic copolymers; degradation; thermogravimetric analysis; activation energy

INTRODUCTION

Cellulose is a semicrystalline material with regions of high microcrystalline and amorphous regions. In the crystalline regions, the polymer chains adopt parallel positions in a monoclinic lattice.[1]

The strength of cellulose is attributable to its fibrous composition, which results from the hydrogen bonding within the chain, maintaining a linear conformation and hydrogen bonding between cellulose chains, assisting in fibril formation. Degradation of cellulose involves the breaking of covalent bonds within and between monomer units in the chain and the loss of inter- and intrachain hydrogen bonds. Chemical modification of cotton by grafting with vinylic monomers allows us to obtain new materials with different structural characteristics, which can be reflected in their thermal decomposition process. The thermal behavior of these cellulosic materials was studied by differential scanning calorimetry (DSC) in previous work (see ref. 3).

EXPERIMENTAL

Materials

All materials considered in this paper were prepared as described previously.[2] In this paper, the hydrophilic cotton, purified with chloroform, ethanol and a 1% NaOH solution, was called Cel.A. Following this process, mercerized cotton cellulose was prepared by treatment with NaOH solu-

Table I Crystallinity Index CI, Viscosimetric Average Molecular Mass ($\bar{M}_v$) and Average Polymerization Degree $\overline{PD}$ for Native and Cotton Cellulose Mercerized with Different Percentage of NaOH

Sample	% NaOH	CI	$\bar{M}_v$	$\overline{PD}$
Cel.A	0	0.68	340,209	2088
Cel.B	10	0.58	279,741	1722
Cel.C	15	0.53	267,791	1650
Cel.D	20	0.49	263,075	1621

tions (10, 15, and 20%), called Cel.B, Cel.C, and Cel.D, respectively (Table I).

The vinylic-grafted copolymers of cellulose were prepared by graft copolymerization of vinyl acetate (VA) and methyl acrylate (MA) on cotton cellulose initiated by the Ce(IV) ion system, using different volumetric ratios of monomers V_{VA}/V_{MA} and different cellulosic substrates.[2]

For thermogravimetric study, we selected the following cellulosic vinylic copolymers: Series C, copolymers with the same cellulosic substrate (Cel.C) but different volumetric ratios V_{VA}/V_{MA} and Series 1, copolymers with different cellulosic substrate but the same volumetric ratio of monomers. The grafting percentage $\% G$ (Table II) was calculated as follows:

$$\% \, G = \frac{\begin{array}{c}\text{dry mass of grafted sample–}\\ \text{dry mass of original sample}\end{array}}{\text{dry mass of original sample}} \times 100 \quad (1)$$

The grafting percentage is attributable to the grafting frequency GF (number of vinylic chains per number of cellulosic chains) and/or to the length of the vinylic grafted chains. In our previous work,[2] we established that the GF decreases in the copolymers in the following order: CA1 > CC1 > CD1 > CC2 > CC3, and the vinylic length decreases as follows: CD1 > CC1 > CC2 > CC3 > CA1.

Thermogravimetric Analysis

Thermogravimetric analysis was carried out by a thermogravimetric analyzer TG-50 module with a microbalance Mettler M3 coupled to a Mettler Thermoanalyzer TA-400. In dynamic experiments, the heating rates were 5, 10, 15, and 20°C/min under nitrogen atmosphere (flow rate 200 mL/min). The interval of temperatures was from 25 to 600°C. The sample masses were about 7–8 mg.

RESULTS AND DISCUSSION

Celluloses

The thermogravimetric (TG) curves and derivative thermogravimetric (DTG) of the cellulosic samples at heating rate 10°C/min are shown in Figure 1. Two main stages are observed. The first one, between 25 and about 150°C, is attributed to the loss of moisture absorbed by the cellulose sample. The second stage, beginning at about 280–290°C, is attributed to the main decomposition process. The percentage of the mass loss attributable to the sample moisture, as well as the percentage mass loss of decomposition of the dry sample, have been determined in the investigated temperature interval (Table III).

The loss of mass in the first stage is between 4 and 8%. It is shown that the mass of absorbed water is higher in the celluloses with less crystallinity, which corresponds to the results obtained by DSC.[3] This shows the different hygroscopic character of celluloses, attributable to the fact that the absorbed moisture occurs in the amorphous regions, and its quantity is directly related to the number of free hydroxylic groups.[4–6]

Concerning the main decomposition process, the temperatures T_i and T_f at which the decomposition begins and ends, respectively, and the decomposition temperature interval ΔT have been determined. The average mass loss in the second stage has been determined as the ratio of the decomposition mass loss and the temperature interval in which it has taken place (Table III).

Table II Vinylic Copolymers of Cellulose: Percentage of Grafting, Cellulosic Substrate and Volumetric Ratio of Monomers V_{VA}/V_{MA} Used in their Preparation

Sample	% Grafting	Cellulosic Substrate	V_{VA}/V_{MA}
CC3	33	Cel.C	90/10
CC2	53	Cel.C	85/15
CA1	63	Cel.A	80/20
CC1	170	Cel.C	80/20
CD1	305	Cel.D	80/20

Figure 2 Dependence of the temperature T_α on decomposition degree α for celluloses mercerized with different percentage of NaOH (0, 10, 15, and 20%).
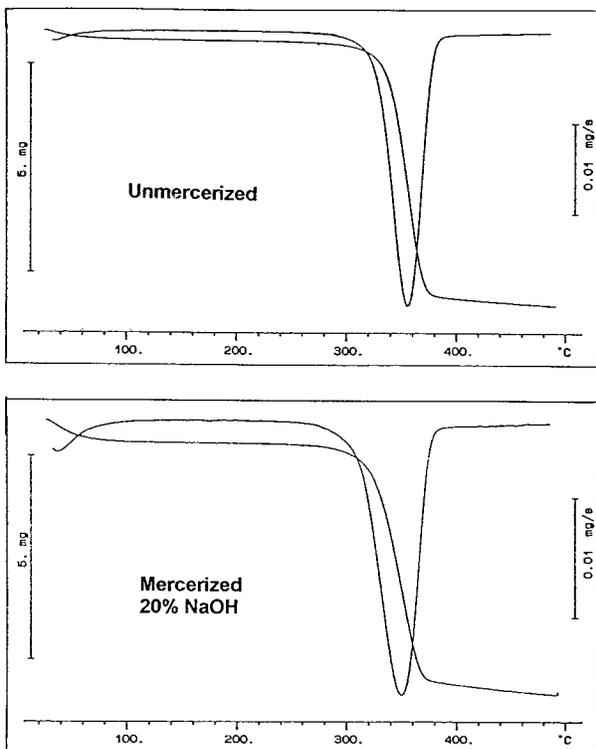
Figure 1 TG and DTG curves of celluloses at heating rate 10°C/min.

The decomposition mass loss has been calculated from the dried sample as follows:

$$\% \text{ mass loss} = (m_i - m_r) \times 100/m_i \qquad (2)$$

where m_i is initial mass of dry sample, and m_r is the mass of the residue.

According to these results, unmercerized cellulose begins to decompose at the highest temperature T_i. This temperature decreases as the mercerization degree increases; simultaneously, the temperature interval ΔT of the process increases, while the average mass loss decreases, showing
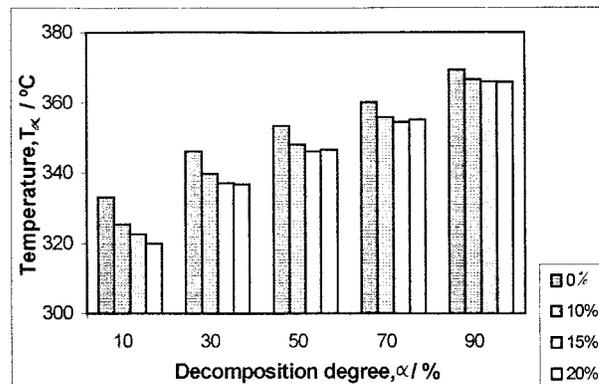
that the crystallinity of cellulose samples affects the over-all kinetics of degradation.

As is known, the degradation rate is the most rapid in the amorphous regions between the areas of high crystallinity. The degradation rate is not uniform within the amorphous regions, and in some areas, it is higher than in the others.

Although, in our previous work,[3] we identified two stages of cellulose degradation as two endothermic peaks on the DSC curve, only one stage, which can include both stages of cellulose degradation, is shown in the TG curves. The first stage of the cellulose degradation, between 240 and 300°C, shown by DSC, is attributed to the depolymerization of the chain and perhaps to some loss of water molecules from the primary OH groups. It seems that it represents only a slight mass loss, and it is not observed by thermogravimetric analysis.

The decomposition degree α has been calculated as follows:

$$\alpha = (m_i - m_\alpha) \times 100/(m_r - m_i) \qquad (3)$$

Table III TGA Dates of Celluloses

Sample	% NaOH	Mass Loss in 1st Stage (%)	T_i (°C)	T_f (°C)	ΔT	Mass Loss in 2nd Stage (%)	Average Mass Loss in 2nd Stage (%/°C)
Cel.A	0	3.52	297.8	385.0	87.2	90.05	1.03
Cel.B	10	4.25	290.0	386.3	96.3	89.91	0.93
Cel.C	15	5.22	280.0	386.0	106.0	86.92	0.81
Cel.D	20	7.84	260.0	388.0	128.0	85.20	0.66
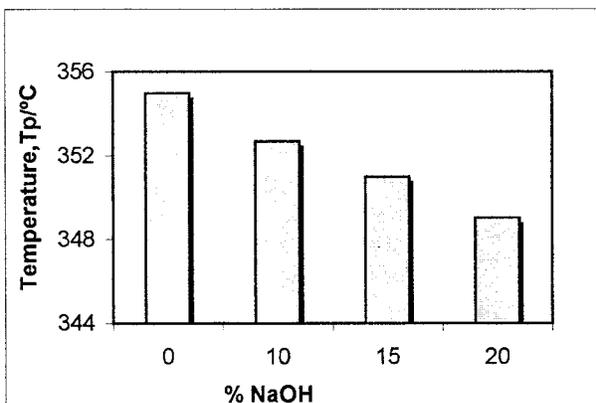
Figure 3 Dependence of the peak temperature T_P on the percentage of NaOH at 10°C/min.

only one process of decomposition, although the decomposition must be more complex. The linear relationship $\ln(q/T_P^2)$ versus $(1/T_P)$ is observed; therefore, it seems that Kissinger's method is satisfactory for determining the apparent activation energy of cellulose thermal degradation. Our results are shown in Table IV.

The activation energy decreases as the % NaOH in the mercerized cellulose increases, and the high value of E_a for the unmercerized sample reveals some important structural differences between unmercerized and mercerized celluloses. All these results indicate that the NaOH causes some structural differences between the amorphous regions of cellulose-I (unmercerized) and cellulose-II (mercerized).[8] It can be also shown that by the NaOH treatment[9] the amorphous amount of the material increases at the same time the crystalline ratio of the material achieves the most perfect order.

where m_α is mass at α decomposition degree.

Temperatures T_α at different degradation degrees of each cellulose sample are shown in Figure 2. It can be seen that the unmercerized cellulose (Cel.A) has a higher T_α. For the mercerized samples, T_α decreases as the mercerization increases, and the differences become less important for higher percentages of NaOH.

Activation Energy of Cellulose Degradation

The peak temperature T_P on the DTG curves are those temperatures at which the rate of degradation reaches the maximum value. In Figure 3, it can be seen that the T_P (at 10°C/min) decreases as the mercerized degree of the sample increases; that is, by increasing the amorphous character of the cellulose sample. The crystallinity of the sample decreases simultaneously.

We considered the T_P temperatures at different heating rates for each sample, and from these values, the apparent activation energy E_a has been calculated following Kissinger's method.[7] It has been assumed that DTG peak corresponds to

Vinylic Copolymers of Cellulose

The TG and DTG curves of the vinylic cellulosic copolymers show three main stages of mass loss (Fig. 4). The first, between 25 and 120°C, is attributed to the loss of moisture. It is observed that the copolymer CA1 has the lowest percentage of absorbed water, corresponding to the most crystalline cellulosic substrate with more OH hygroscopic groups in the hydrogen bonds.

The other two stages from about 280 to 500°C are attributed to the thermal decomposition; the first one is more important. The characteristics of the thermal decomposition of the vinylic copolymers of cellulose and poly(vinyl acetate) (PVA) are shown in Table V. The decomposition percentage of mass loss has been calculated from the dried sample according to Eq. (2).

All of the copolymers begin to decompose at higher temperatures than their cellulosic substrate and PVA; in other words, the copolymers

Table IV   Peak Temperatures T_P at Different Heating Rates q, and Apparent Activation Energy E_a for Thermal Degradation of Cellulosic Samples Calculated by Kissinger's Method

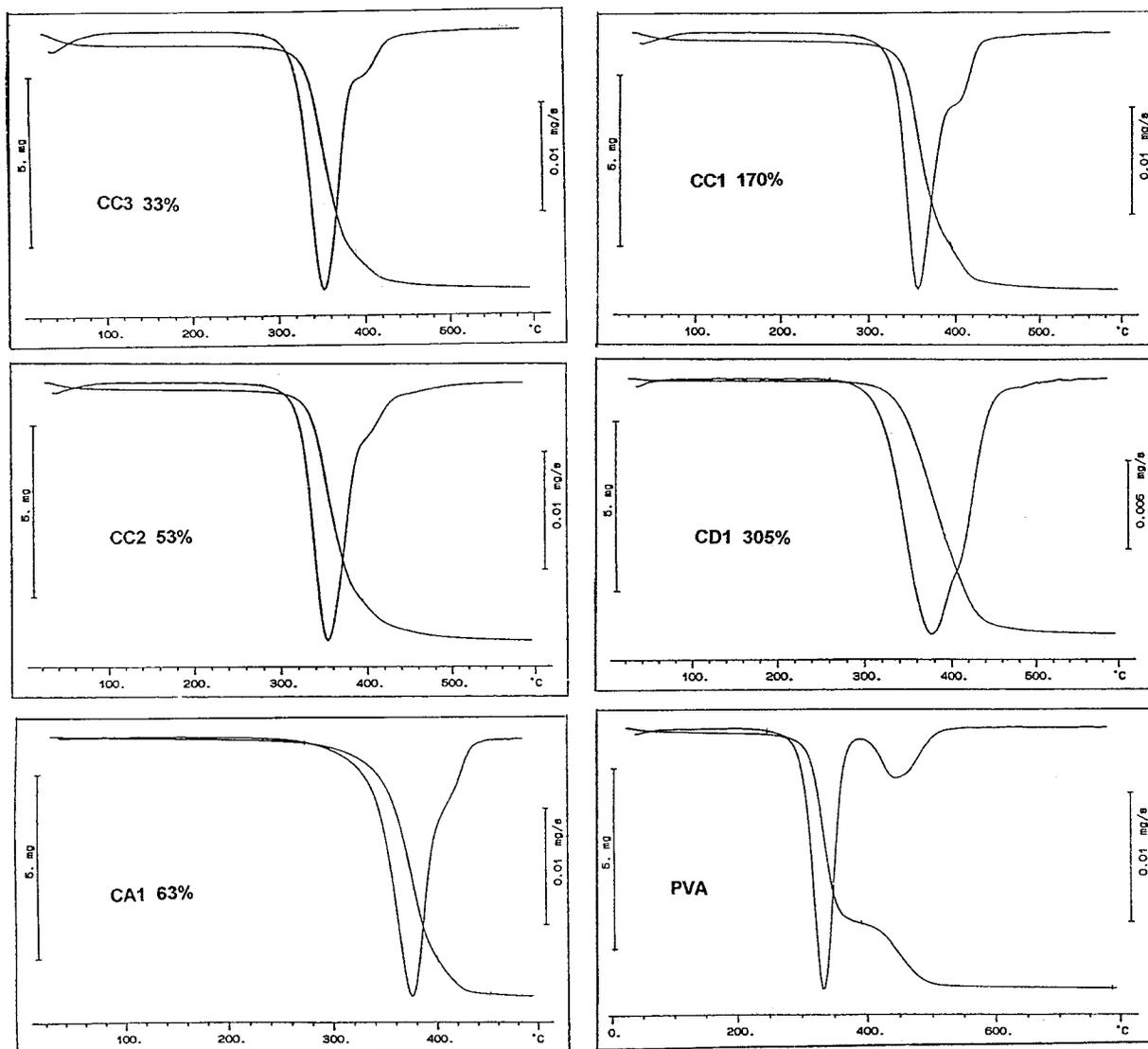| q (°C/min) Sample	Temperature, T_P (°C)				E_a (kJ mol^{-1})
	5	10	15	20	
Cel.A (0%)	352.7	355.0	356.1	357.0	1138.5
Cel.B (10%)	346.0	352.7	356.4	359.6	328.2
Cel.C (15%)	345.0	351.0	357.5	363.0	193.6
Cel.D (20%)	335.3	349.0	360.0	365.7	134.5

Figure 4 TG and DTG curves of vinylic cellulosic copolymers and PVA at heating rate 10°C/min.

indicate higher thermal stability. The percentage mass loss in the first degradation stage of the copolymers is lower that of the cellulosic substrate, but the percentage mass loss of the total process is higher.

As it is known, in thermal decomposition of PVA, the first stage is attributed to the loss of CH_3—COO^- group ($T_i = 281.0°C$) and the second stage ($T_i = 390.7°C$) to the loss of —CH_2—CH— groups.[3] PVA is the major component in the grafted vinylic chains onto cellulose. Although some poly(methyl acrylate) PMA must be incorporated in the chain, no effects have been detected in the present study.

The percentage mass loss for the first and the second stage of the decomposition process, as well as for the total process (Table V), gives some interesting information. In the first stage, PVA has a 68.62% mass loss, which is the same as calculated mass percentage of CH_3—COO^- groups in the PVA chain; therefore, these groups should be lost as volatile compounds. In the second stage, the 23.92% mass loss added to the 7.46% of residue, gives 31.38%, which is the same as the calculated percentage of —CH_2—CH— groups (31.39%) in the PVA chain; thus, this stage results from the decomposition of the vinylic chains.

Table V   Characteristics of the Thermal Degradation of Vinylic Copolymers of Cellulose and PVA at Heating Rate 10°C/min

Sample	% G	Stage	T_i (°C)	T_f (°C)	Mass Loss (%)	Residue (%)
CC3	33	1st	300.0		80.00	
		2nd	383.3		12.86	
		Total	300.0	450	92.86	7.14
CC2	53	1st	302.6		78.49	
		2nd	396.0		14.39	
		Total	302.6	450	92.85	7.17
CA1	63	1st	302.0		75.31	
		2nd	398.0		14.80	
		Total	302.0	460	90.11	9.89
CC1	170	1st	318.0		78.08	
		2nd	395.0		16.27	
		Total	318.0	450	94.35	5.65
CD1	305	1st	300.0		61.30	
		2nd	395.0		32.44	
		Total	300.0	450	93.74	6.26
PVA	——	1st	281.0		68.62	
		2nd	390.7		23.92	
		Total	281.0	550	92.54	7.46

We can assume that the mass loss in the first stage of the cellulosic vinylic copolymers decomposition is attributable to both processes: the cellulosic substrate decomposition and the loss of the acetate groups. It increases as the cellulose amount increases and percentage G decreases in Series C. In Series 1, not only the percentage G must be considered but also the different cellulosic substrates. In the second stage, which is attributed to the vinylic chains —CH_2—CH— loss, the mass loss increases as percentage G increases, as it was expected.

For the total process of decomposition, the mass loss of 93–94% is observed for all the copolymers, except CA1 (90.11%), which must be attributable to the unmercerized cellulosic substrate and the effects of grafting. The highest residue of this sample is the consequence of poorer decomposition and higher thermal stability.

For each stage of decomposition, the temperatures T_α at the given decomposition degree α have been determined. It is observed for Series C that T_α temperatures increase as % G increases (Fig. 5). It seems that the amount of grafting makes the degradation more difficult, so the copolymers become more thermostable.

In Figure 6, the effects of cellulose substrate and of percentage G on T_α values for Series 1 are shown, according to the hypothesis that in this stage of decomposition, both cellulose and

CH_3COO^- groups degrade. CA1 copolymer shows the highest T_α (except for $\alpha = 10\%$) in accordance with the high crystallinity of the cellulosic substrate despite its low percentage G. The T_α temperatures of CC1 copolymer are lower than those of the CA1, which might be a consequence of a less crystalline substrate in this sample, despite its percentage G being higher than that of CA1. The CD1 copolymer, with the least crystalline sub-
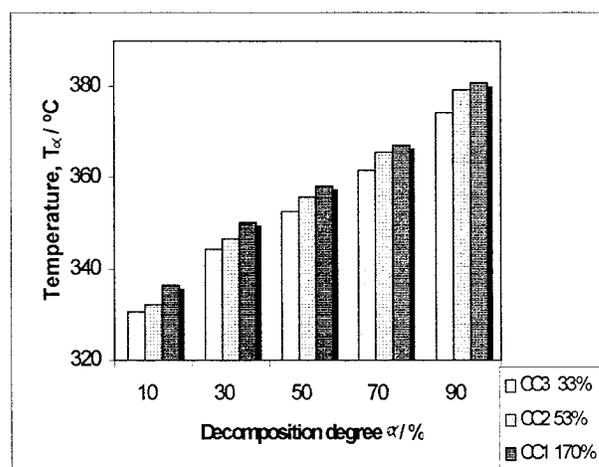

Figure 5   Dependence of temperature T_α on decomposition degree α for cellulosic copolymers of the series C with different grafting percentages (33, 53, and 170%).
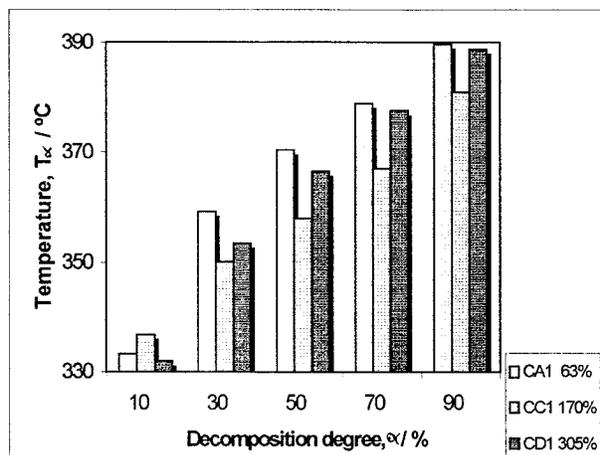
Figure 6 Dependence of temperature T_α on decomposition degree α for the cellulosic copolymers of Series 1 (effects of percentage G and of cellulosic substrate).

strate and very high percentage G, shows T_α higher than for CC1, which is because of the great amount of grafting. At the same time, the shape of its DTG peak shows that complex processes in the stage of decomposition are included, as has been noted by other authors.[10]

Although it is difficult to determine T_i temperature accurately for the second stage on the thermograms, it is evident that this T_i is higher than the T_f of celluloses. The T_i temperatures of the second degradation stage of vinylic copolymers are similar to the T_i of the second degradation

stage of PVA. Therefore, it can be assumed that the second stage of vinylic copolymers is attributable to the decomposition of the vinylic grafted chains —CH_2—CH—.

The ratio of 90% mass loss and the temperature interval $(T_{90\%}-T_i)$ in which the mass loss of 90% takes place for each stage and for the total process has been calculated (Table VI) to obtain more information. In the first stage (cellulose and acetate groups degradation), the ratio decreases as percentage G increases (except for CC1), showing that the process becomes more difficult. In the second stage (vinylic chains degradation), it seems that the grafting frequency is responsible for the following: the weight loss increases as GF increases, which must be attributable to the fact that the second stage begins when the cellulose substrate is still being degraded and the amount of the end groups in the vinylic chains is higher for high GF copolymer; thus, making its degradation easier.

The theoretical residue r_{th} in Table VI, is obtained for the blends of cellulose and PVA in the same mass percentage as the percentage G of cellulosic copolymers is. The residue of the blends is calculated as the sum of cellulosic residue and the vinylic chain residue, because the residue of the cellulosic copolymers degradation comes from cellulose and vinylic chains:

$$\% \, r_{th} = (m_c \times r_c + m_{vp} \times r_{vp}) \times 100/m_{c+vp} \quad (4)$$

Table VI Temperature at Which Mass Loss is 90%, $T_{90\%}$, and the Average Mass Loss in the Temperature Interval $(T_{90\%}-T_i)$ for the First and Second Degradation Stage and for Total Process

Sample	% G	Stage	$T_{90\%}$ (°C)	Average Mass Loss (%/°C)	Theoretical Residue, r_{th} (%)
CC3	33	1st	374.3	1.21	
		2nd	473.5	0.99	
		Total	399.8	0.90	11.03
CC2	53	1st	379.4	1.17	
		2nd	484.7	1.01	
		Total	408.5	0.85	9.89
CA1	63	1st	389.6	1.03	
		2nd	428.8	2.92	
		Total	407.8	0.85	7.01
CC1	170	1st	380.9	1.43	
		2nd	457.9	1.43	
		Total	406.2	1.02	6.62
CD1	305	1st	388.7	1.01	
		2nd	442.8	1.88	
		Total	424.1	0.73	5.42

Table VII   Peak Temperature T_P at Different Heating Rates q (5, 10, 15, and 20°C/min) and Apparent Activation Energy E_a Calculated by Kissinger's Method for the Main Degradation Peak of Vinylic Copolymers of Cellulose

Sample	% G	% Cell.[a]	Temperature T_P (°C)				E_a (kJ/mol)
			q/5	10	15	20	
CC3	33	75.2	340.0	350.4	357.0	369.0	146.53
CC2	53	63.5	341.0	354.0	360.0	365.0	176.23
CA1	63	61.3	363.0	375.0	383.0	387.0	187.06
CC1	170	37.0	349.0	356.3	362.3	367.0	240.14
CD1	305	24.7	363.0	375.0	383.0	387.0	187.06

[a] % cellulose = (cellulose mass/copolymer mass) $\times$ 100.

where m_c is cellulose mass, m_{vp} is vinylic polymer —(CH—CH$_2$)$_n$— mass, m_{c+vp} is blend mass, and r_c and r_{vp}, respectively, are the residue of cellulose (Cel.A, Cel.C, or Cel.D) and the residue of the vinylic polymer PVA (the values are in Table V).

The theoretical residues of the blends degradation decrease as the vinylic percentage increases in all cases, in contrast to the copolymers. It is higher than the residue of the corresponding cellulosic copolymer in Series C; whereas, it is lower for the CA1 and CD1 copolymer. This shows that the amount of solid products at the end of the cellulosic vinylic copolymers degradation depends, not only on the vinylic percentage, but also on the chemical bonds between cellulose and vinylic chains.

Activation Energy of Thermal Degradation of Copolymers

The apparent activation energy has been calculated by Kissinger's method using the main peak temperature on the DTG curves obtained at different heating rates. The values of E_a are shown in Table VII.

Although the same values of T_P, and, consequently, the same E_a, are observed for both CA1 and CD1 copolymers, the shape of their TG and DTG curves differs (Fig. 4a,b), which is attributed to the differences in cellulosic substrate and grafting percentage.

The apparent E_a of copolymers with lower percentage G is lower than the E_a of their cellulosic substrate (Table IV), but for the copolymers with the highest percentage G, E_a is higher than E_a of cellulosic substrate. It might be assumed that grafting favors degradation, but if the amount of vinylic polymer is too high, the process (which

must include cellulose and CH$_3$—COO$^-$ groups degradation) requires more energy.

In Figure 7, it can be seen that E_a increases as the percentage G increases for series C. The thermal stability of the vinylic copolymers with the same cellulosic substrate also increases as a consequence of the GF increase and the increase of the length of the vinylic grafted chains. The values of E_a of vinylic cellulosic copolymers in Series 1 are related not only to the percentage G, but also to different cellulosic substrates. Therefore, the CD1 copolymer shows higher E_a than its cellulosic substrate (Cel.D) because of the large amount of grafting with long chains and high GF. On the other hand, the E_a of CA1 is very much lower than E_a of its cellulosic substrate. The percentage G in this sample is low, with short vinylic chains, but high GF. Nevertheless, the large de-
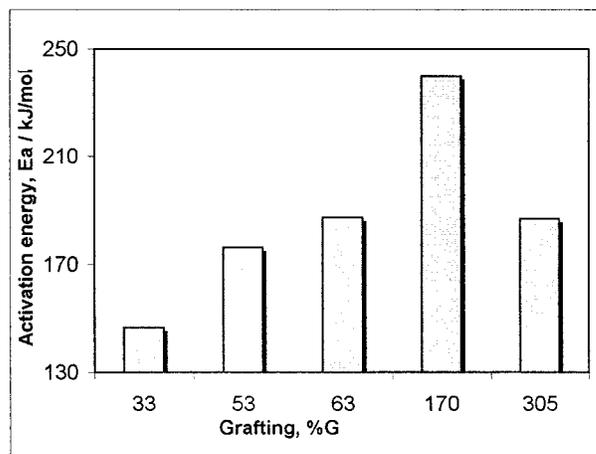

Figure 7   Dependence of the activation energy E_a of the copolymers main degradation stage on the grafting percentage G.

crease of the E_a for the CA1 copolymer in relation to Cel.A may indicate, not only the influence of the grafting, but also some structural changes in the initial native cellulose during the grafting reaction. The very high E_a as well as the T_i of the CC1 copolymer shows that grafting onto mercerized cellulose with 15% NaOH (170% of grafting) makes it more thermostable, with low residue percentage at the end of the degradation and shorter temperature interval of the degradation.

CONCLUSIONS

- The thermal stability of native (unmercerized) cellulose is higher than the stability of mercerized celluloses.
- The thermal stability of the mercerized celluloses decreases as the percentage NaOH increases, because of the increase of its amorphous character.
- On the DTG curves of vinylic cellulosic copolymers, two main degradation stages have been observed. The first is attributed to both the decomposition of cellulose and the decomposition of CH_3COO^- groups from grafted vinylic chains and the second to the —CH_2—CH— chains decomposition.
- The thermal stability of vinylic copolymers of celluloses depends upon cellulosic substrate crystallinity that increases as the crystallinity increases. It also depends upon grafting percentage; therefore, the thermal stability increases as percentage G decreases for the

same cellulosic substrate and increases as the grafting frequency increases.

Considering all these factors, it is possible to prepare cellulosic materials (as CC1 copolymer) with high thermal stability and, at the same time, a short temperature interval of degradation and a small residue. This is interesting, because these materials may have good stability during their practical applications and cause few environmental problems when they are no longer in use.

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