Thermal Behavior of Ungrafted and Grafted Bagasse and Wood Pulps

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SYNOPSIS

The effect of grafting of methyl methacrylate (MMA) and acrylonitrile (AN) on the thermal behavior of the pulp of sugar cane loaded with $CaCO_3$ and the pulp of a broad-leaved tree has been studied by thermal methods. Different experimental conditions of grafting AN onto the eucalyptus pulp have been used, including both water and organic solvent systems as the medium of reaction. To optimize the grafting of MMA onto wood pulp, the effect of pulp swelling and the contact time of the monomer with the pulp have been examined. Ungrafted as well as grafted cellulose samples with different levels of grafting were characterized by differential scanning calorimetry (DSC) and the thermogravimetric analysis (TGA). The $CaCO_3$ filler makes the pulp of bagasse thermally more stable. The grafting of MMA onto the bagasse or the wood pulps improves their thermal stability. This is not the case for wood grafted with poly(AN). The thermal stability of the grafted and ungrafted samples varies after a few weight percent has been lost. The glass transition temperature (T_g) of the copolymers have been measured and they are in good agreement with the calculated data. © 1993 John Wiley & Sons, Inc.

I. INTRODUCTION

There is considerable industrial and academic interest in cellulose fiber modification. It includes the improvement not only of their physical and mechanical properties, but also of their thermal properties. Several chemical reactions have been investigated to improve the properties of cellulose fibers.[1] One of the most extensively studied methods is the graft copolymerization of some vinyl monomers onto cellulosic substrates.

In grafting, a covalent chemical bond is formed between the cellulose backbone and the guest polymer, making the product a permanent "new" substrate.[2] A large number of papers have been published on different methods of synthesizing graft copolymers of cellulose.[3] Graft copolymerization of vinyl monomers onto various cellulosic materials, such as cotton and microcrystalline cellulose, have been studied,[4] in contrast to loaded pulp of bagasse, pulp of broad-leaved trees, and eucalyptus, which have been rarely or never studied.

The objective of this work was, on the one hand, to optimize the grafting of methyl methacrylate (MMA) and acrylonitrile (AN) onto pulp of bagasse and wood using different media, using different systems of initiation, and by studying two important parameters: the pulp swelling and the contact time of monomer with pulp. On the other hand, the purpose of this work was to gather information on the thermal stability of the cellulosic graft copolymers. Both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been used.

II. EXPERIMENTAL

Cellulosic Materials

The cellulosic fibers used in this study were bleached pulps from wood and bagasse. The four samples investigated were kindly supplied by the laboratory of

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Agroressource of E.N.S.C. of Toulouse and the Cellulose d'Aquitaine company of Saint Gaudens.

They have the following characteristics:

Cell I: The pulp from bagasse (sugar cane) that contains cellulose 95.81%, lignin 2.64%, pentosan-c 0.99%, NaOH 0.56%, and water.

Cell II: The pulp from sugar cane. It is loaded with 5–7% of $CaCO_3$.

Cell III: The pulp from eucalyptus wood. Cells III and I have the same composition.

Cell IV: The pulp from a broad-leaved tree. Cellulose is the major component; there is no lignin.

Solvent for Cellulose

Dimethylacetamide (DMAC), containing 9% of lithium chloride, has been reported to be an excellent, nondegrading solvent for cellulose.[5] This solvent has been used here for the preparation of different cellulose solutions.

Differential Thermal Analysis

DSC experiments were carried out on a Setaram DSC 92 apparatus equipped with a CS92 controller, a DSC92 calorimeter, as well as a PC92 computer. Each sample undergoes a programmed temperature variation, in the range 25–350–25°C. The glass transition temperature, T_g, and the change of the heat capacity, ΔC_p, have been determined for the pulps of different origins. The T_g can be detected only when the temperature is decreased from 300 to 25°C.

Tg and ΔC_p data are given in Table I. Thermogravimetric measurements were carried out with an TGA92 apparatus. The thermogravimetric assembly TGA92 is made of the thermobalance itself (balance, furnace, gas circuit and power), a controller, and a PC92 computer.

Viscosity and Characteristics of the Cellulose

The intrinsic viscosities $[\eta]$ of the various samples were determined by extrapolation to $C = 0$ of the reduced specific viscosities $(\eta - \eta_0)/(\eta_0 C)$ measured with an Ubbelohde viscometer at 30°C ± 0.1. η, η_0, and C have the usual meaning. An example of the determination of the intrinsic viscosity in the case of cell I is given in Figure 1. The weight-average molecular weights were calculated with the constants reported by Mc Cormick et al.[6] for cellulose solutions in DMAC/LiCl:

$$[\eta] = (1.278 \times 10^{-4}) Mv^{1.19} (\mathrm{cm}^3/\mathrm{g})$$

The data for the four cellulose samples are given in Table II.

Table I Thermal Characteristics of the Cellulose Samples

Cellulose	T_g (°C)	ΔC_p (J/g°C)
Cell I	244.36	12.524
Cell II	245.43	0.020
Cell III	244.01	6.467

Other Chemicals

AN and MMA monomers used for graft copolymerization were obtained from Merck and Prolabo, respectively, and purified by distillation. The central fraction was collected and stored in a refrigerator in dark bottles.

Ceric ammonium nitrate (CAN) was obtained from Merck, and cerium IV sulfate and ammonium persulfate (APS) reagent grade, from Prolabo. Dimethylacetamide (DMAC) and lithium chloride (LiCl) were obtained from Sigma. Paraformaldehyde (PF), obtained from Janssen, was dried in a desiccator over $CaCl_2$. All the other chemicals, also of analytical grade, were used as supplied by the manufacturers.

Ungrafted and grafted pulps were characterized by infrared spectroscopy. Spectra were recorded on a Perkin-Elmer model 1600 FTIR spectrophotometer with the KBr pellet technique.

Grafting Procedures on Pulps

Graft Copolymerization of AN on Pulp from Eucalyptus (Cell III) in DimethylSulfoxide–Paraformaldehyde (DMSO–PF)

The method described by Nishioka and Kosai[7] was used for the graft copolymerization. The cellulose sample (2 g) was introduced into a flask containing 100 cm^3 of DMSO and 2.4 g of PF. The mixture was kept at 130°C under vigorous stirring. The dissolution of cellulose was allowed to proceed for 15 h. After the dissolution of cellulose, the solution was poured in a 250 cm^3 four-necked glass reactor equipped with a mechanical stirrer, condenser, thermometer, and gas inlet tube for N_2 bubbling. Appropriate amounts of the DMSO solution and initiator were mixed at a temperature lower than 20°C, (APS: 0.8 g/100 g of DMSO solution); meanwhile, dried nitrogen was bubbled through the mix-

ture; the required amount of monomer was added (AN: 4 g/100 g of DMSO solution). The polymerization was carried out at 40°C and was stopped 5 h later by adding hydroquinone. Then, the polymerization mixture was poured into distilled water with vigorous stirring and filtered on a sintered glass crucible; the solid residue was dried at 40°C. The crude graft product was treated in a Soxhlet apparatus for 27 h to extract ungrafted polyacrylonitrile with dimethylformamide (DMF).

Graft Copolymerization of AN on Pulp from Eucalyptus in Water

The graft copolymerization was adapted from the method previously described by Richards[8] using cerium IV sulfate as initiator. Cellulose (2.404 g) was immersed in 80 mL of water with 4 mL of AN. The mixture was stirred for 30 min and the nitrogen was bubbled throughout the system. Two parts of fresh catalyst solution were prepared by dissolving 0.849 g of cerium IV sulfate $Ce(SO_4)_2$, $4H_2O$ (0.1*M*) in 1.5 mL of 1*N* nitric acid (HNO_3). The temperature of the reaction was adjusted to 20°C. The mixture was reacted during 2 h and, afterward, the second part of the initiator was added. The polymerization was continued during another 2 h period and stopped. The residue was washed with (2 × 200 mL of DMF at 100°C) and methanol and dried in air at room temperature.

Graft Copolymerization of AN onto Wood Pulp from Broad-leaved Trees in Water

The same method as that previously described was used, but the initiator (CAN) was added in just one part. The reaction was continued during 1 h.

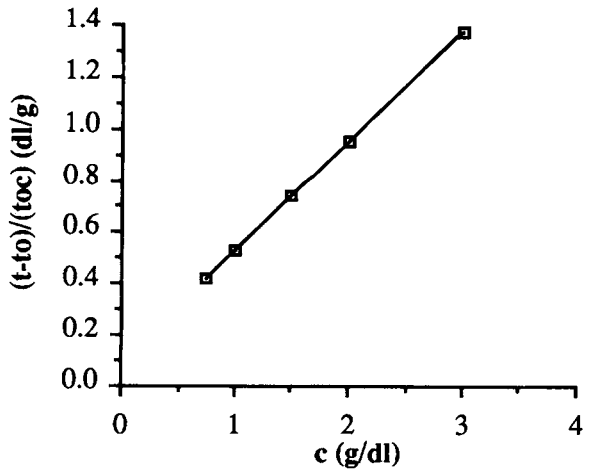

Figure 1 Intrinsic viscosity of cell I.

Table II Characteristics of the Cellulose Samples

Cellulose	Solvent	[η] (dL/g)	M_v	*DP*
Cell I	DMAC/LiCl	0.104	13,400	74
Cell II	DMAC/LiCl	0.404	41,800	232
Cell III	DMAC/LiCl	0.113	14,300	80
Cell IV	DMAC/LiCl	0.201	23,000	127

Graft Copolymerization of MMA onto Wood Pulp (Broad-leaved Trees) in Water

The reaction was based on the method reported by Hebeish and Mehta.[9] Grafting was carried out using 2 mL of monomer per gram of pulp and distilled water (95 mL) at 25°C; N_2 was bubbled in the reactor during 30 min, then the initiator was added (0.52 g of 2.5 × 10^{-3} mol/L of CAN in 1.5 mL of 1*N* HNO_3). The reaction was continued for 2 h. The polymerization was quenched by washing the product with acetone.

Grafting of PMMA on Sugar Cane Pulp Loaded with $CaCO_3$

The wet pulp corresponding to 3.99 g of dry pulp was reacted with 6.5 mL of MMA and 150 mL of water at 40°C under N_2 for 20 min.

A fresh solution of 0.2 g of CAN in 1.8 mL of 1*N* HNO_3 was added to the mixture. The reaction was kept under N_2 for 1 h under stirring (220 rpm). The reaction was stopped by adding hydroquinone. The grafted cellulose was precipitated in a great excess of CH_2Cl_2, as the homopolymer is soluble in that solvent. The residue was filtered and dried at 40°C.

III. RESULTS AND DISCUSSION

Graft Copolymerization onto Cellulose Samples

Grafting with Acrylonitrile

Table III gives the results of microanalysis for AN grafted on pulp from eucalyptus (cell III) obtained by copolymerization in homogeneous DMSO–PF solution. Using microanalysis data, the grafting ratio PG (%) can be expressed as follows:

$$PG = (X/Y) \times 100$$

Table III Characteristics of the Copolymer

Cellulose	% N	% O	*X*	*Y*	PG (%)
Cell III	5.733	37.045	21.7	68.7	32

Table IV Effect of the Nature of the Medium on the Grafting onto Cell III

Cellulose	Medium	PG (%)
Cell III	DMSO/PF	32.0
Cell III	H_2O	79.0

where X is the quantity of nitrogen contained in the copolymer sample, $X = \%(N) \times$ (weight of monomer of AN/14), and Y is the quantity of oxygen contained in the copolymer sample, $Y = \%(O) \times$ [weight of one sugar unit)/(6 × 16)]. The grafting ratio obtained was about 32%.

Suspension copolymerization of AN on the same cellulose (cell III) in water has also been carried out. The infrared spectrum of the grafted copolymer showed the characteristic peaks of the homopolymers. This indicates that PAN was effectively grafted onto the cellulose backbone.

The grafting efficiency can be also described by data defined on a weight basis as

grafting yield [PG(%)]

= (polymer in graft/weight of substrate) × 100

= (weight of the grafted cell

− weight of the cell)/(weight of cell) × 100

The grafting ratio obtained was about 79%. Table IV summarizes the results obtained for the graft copolymerization of AN in two different media.

Considering the optimum conditions for grafting AN on eucalyptus pulp in both solvents (DMSO/PF and H_2O), the results of the grafting yield suggest that the accessibility of the monomer to the active centers of the cellulose is easier in water than in an organic solvent. Initiation of the grafting polymerization is shown to be a fast, relatively simple process at room temperature. Therefore, grafting reactions were carried out only in water in heterogeneous conditions.

AN has also been grafted onto wood pulp from broad-leaved trees. The infrared spectrum of the graft copolymer after extraction [Fig. 2(a)] shows a peak at 2240 cm^{-1}, which is characteristic for the C≡N group in the PAN chain. The grafting ratio was about 43%.

The radical formation does not depend on the nature of the counterion of the initiator, but on the accessibility to the reacting sites of the wood pulps. The grafting yield for this sample is higher although the reaction time is only 1 h. After a 2 h period, the grafting ratio of AN on the pulps from eucalyptus or from broad-leaved trees does not change any more.

Grafting with MMA

The infrared spectrum of the copolymer (wood pulp-*g*-PMMA) after extraction is shown in Figure 2(b). The presence of a peak at 1700 cm^{-1} is proof of grafting. This procedure gives a grafting ratio equal to 78%. Using ceric ions as initiator, AN and MMA

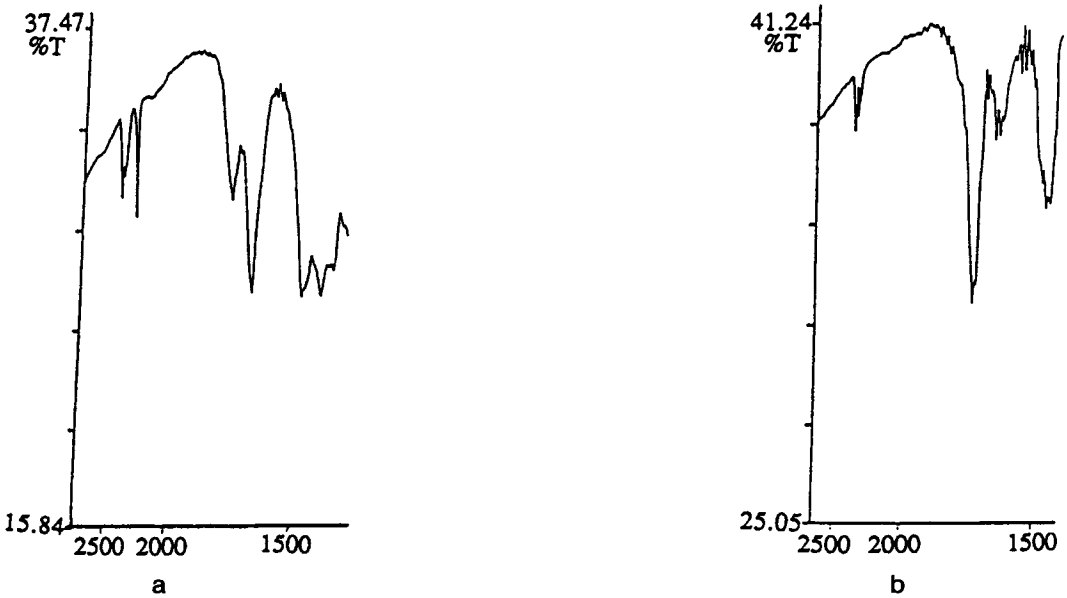

Figure 2 (a) Infrared spectrum of the AN-grafted copolymer; (b) Infrared spectrum of the MMA-grafted copolymer.

are grafted easily on the wood pulp (43% AN grafted in 1 h and 78% MMA grafted in 2 h).

Molecular Weight Determination of the Grafted PMMA. To characterize the polymer graft, the cellulose backbone must be separated from the grafted branches by hydrolysis. Generally, the isolation of the grafted branches from the cellulose backbone is more difficult than from other types of polysaccharide backbones such as starch. The hydrolytic method with 72% sulfuric acid was successfully used for 6 h.[10] The cellulosic backbone was cleaved and PMMA residue was precipitated in water with vigorous stirring, washed repeatedly with methanol, filtered, and dried. The PMMA was purified by dissolving the crude polymer in acetone and subsequently precipitated in methanol. The mean molecular weight of the isolated PMMA grafts was determined from viscosity measurements in acetone at 25°C using the Mark–Houwink–Sakurada equation with $k = 5 \cdot 10^{-3}$ (cm^3/g) and $a = 0.73$.[11] The intrinsic viscosity was found equal to $[\eta] = 39.27$ cm^3/g, corresponding to the mean molecular weight $M_v = 200{,}000$. The frequency of grafting (F_g) defined as the number of moles of grafted PMMA (N_g) per 10^4 anhydroglucose units (AGU) was obtained from the relationship

$$Fg = Ng \times Mo \times 10^4 = (Wg/Mv) \times Mo \times 10^4$$

where Wg is the weight of the grafted PMMA per gram of the pulp and Mo is the molecular weight of one AGU. The found grafting frequency was about 7.

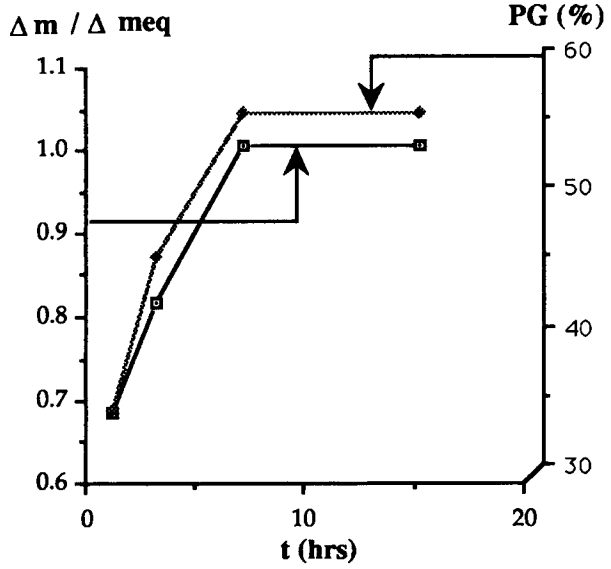

Figure 3 Influence of the swelling time of the pulp. Δm is equal to m (wet sample mass) − m_0 (dry sample mass). Δmeq is the weight at the equilibrium; it is equal to meq (wet sample mass) − m_0 (dry sample mass). Δmeq = 10.13.

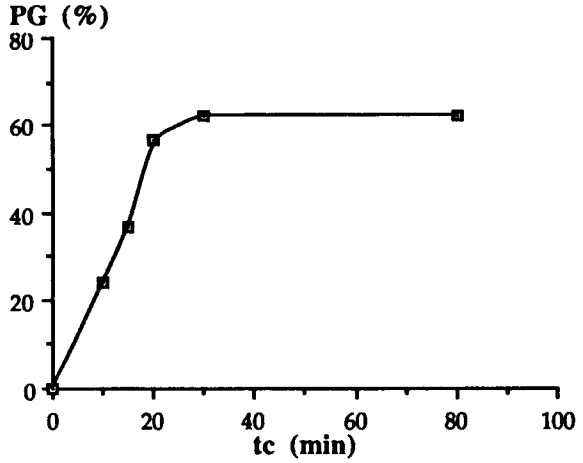

Figure 4 Effect of the contact time on the grafting reaction.

The graft copolymerization process of MMA on sugar cane pulp loaded with $CaCO_3$ is triphasic and limited by mass transfer and by the accessibility of the reagents to the active sites of the cellulose. Therefore, the influence of the swelling time of the cellulose samples on the grafting yield has been investigated. The results are illustrated in Figure 3 where the water ratio in the sample for a given time over water at equilibrium is represented versus time. Maximum grafting is obtained after 7 h of wetting, which corresponds to the maximum of water gain.

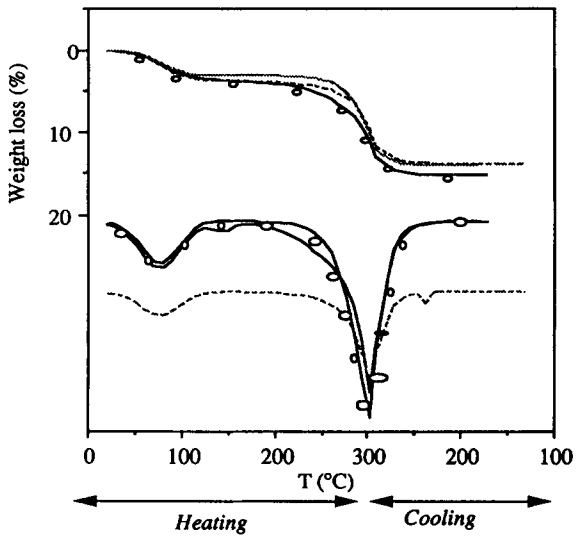

Figure 5 TGA and DTGA curves of pulps: (———) cell I; (. . . . .) cell II; (—ooo—) cell IV. Heating rate = 5°C/min. T(°C): 20–300–20.

Table V Effect of the Cellulose Origin on the Thermal Decomposition

	Dehydration					Pyrolysis				
Sample	T_i[a] (°C)	T_m[b] (°C)	δm[d] (%)	T_f[c] (°C)	δm[e] (%)	T_i[a] (°C)	T_m[b] (°C)	δm[d] (%)	T_f[c] (°C)	δm[e] (%)
Cell I	30.57	76.37	−3.211	133.67	−3.661	174.53	296.73	−12.232	230.00	−10.667
Cell II	30.87	76.53	−3.331	152.17	−3.727	183.40	299.00	−10.319	242.03	−9.527
Cell IV	30.73	76.83	−2.814	139.80	−3.026	175.40	295.50	−10.790	244.63	−11.184

[a] The initial temperature of decomposition of a sample.
[b] The minimum or maximum temperature of the peak.
[c] The final temperature of decomposition of a sample.
[d] The weight loss between T_i and T_m.
[e] The weight loss between T_m and T_f.

The effect of the contact time of monomer with pulp has been also investigated. The monomer is left in contact with pulp at different times: 10, 15, 20, and 30 min. Figure 4 shows the influence of this parameter on the grafting ratio. We notice that PG depends on the contact time. The pulp was left in water overnight before reacting with the monomer. The grafting ratio is optimized when the monomer is left in presence of the pulp for 30 min.

Finally, we observed that the temperature has influence on the MMA grafting reaction on the cellulose II. An increase of 20°C induces a decrease of the grafting ratio of 10%. Indeed, complexation between the Ce^{IV} ion and diol occurs in the first step of the reaction and the complexation constant decreases when the temperature increases.[12]

Thermal Behavior of Cellulose and Cellulose-grafted Copolymers

Extensive thermal analysis studies of cellulosic fibers have been carried out and the effects of crystallinity, orientation, and cross-linking on the pyrolitic behavior of cellulosics have been reported.[13–16] The effects of grafting of various polyacrylates onto cellulose on temperature and heat degradation have been investigated by Kokta and Valde[17] using DSC and TGA. They observed that grafting causes a major shift.

Therefore, we report in this article the thermal properties of cellulose I, II, and IV and cell II grafted with MMA at different grafting levels. This study has also been extended to wood pulp grafted with MMA and AN. The thermogravimetric and the scanning calorimetry analyses provide information on the effect of grafting on the thermal stability of cellulose and on the water content of the samples.

Ungrafted Samples

Thermogravimetry Analysis. Figure 5 shows dynamic TGA curves of cells I, II, and IV and their derivative DTGA. Thermal decomposition of each pulp sample takes place in a programmed temperature range of 20–300–20°C. In the temperature range 30–153°C, dehydration of the samples occurs, and in the temperature range 174–242°C, most of the cellulose is decomposed.

Table V shows the temperature at which the weight loss begins (T_i), the temperature of maximum pyrolysis (T_m), and the temperature of the end of degradation of cellulose (T_f). The three temperatures of dehydration are also given.

The different cellulose samples contain from 6 to

Table VI Temperature of Decomposition at Different Weight Losses of Cellulosic Samples

	Temperature of Decomposition at Different Weight Loss of							
Sample	1%	5%	10%	15%	24%	27%	28%	30%
Cell I	56.7	97.3	242.8	280.7	299.6	286.6	280.8	203.3
Cell II	56.8	92.7	268.1	293.2	286.7	252.8	—	—
Cell IV	61.4	110.7	276.4	293.1	293.7	273.6	232.1	—

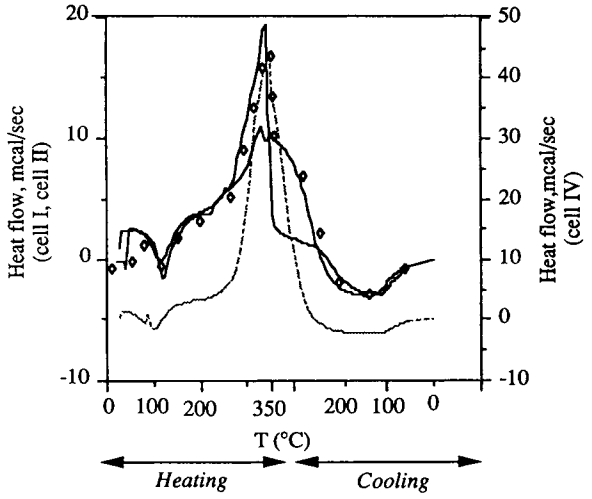

Figure 6 DSC thermograms of pulps: (———) cell I; (. . . . .) cell II; (—▽▽▽—) cell IV. Heating rate = 3°C/min. T(°C): 25–350–25.

7% water. The decomposition of pulp of sugar cane loaded with $CaCO_3$ begins at a temperature higher than that for unfilled cellulose and cellulose from wood. The maximum rate of cellulose pyrolysis occurred at 299, 295, and 297°C for cells II, IV, and I, respectively.

Although the structure of native cellulose fibers remains fibrillar in nature when fillers are added, changes occur. Indeed, the cellulose II lattice is more densely packed than is the cellulose I lattice and the cellulose molecules are more strongly interbound. The slightly higher thermal stability of filled sugar cane can be explained by the additional intermolecular bounding between cellulose and $CaCO_3$.

Table VI shows the decomposition temperature (T_D) at different weight losses for three cellulose samples. Comparing T_D at different weight losses, we can observe that the stability of the cellulose samples differs.

For example: T_D values at 1, 5, and 10% weight losses are higher for wood. T_D values at 15% weight losses are higher for filled sugar cane and wood. Over 24% weight loss, T_D are higher for sugar cane.

Differential Scanning Calorimetry Analysis. The DSC thermograms of ungrafted cellulose (see Fig. 6) were recorded in the programmed temperature range 25–350–25°C. The peak temperature for the corresponding thermograms is given in Table VII.

The DSC curve of cell I shows two peaks: a small endothermic peak in the temperature range 53–191°C, followed by an exothermic peak in the temperature range 230–330°C. The latter splits into two peaks with its peak minimum, respectively, at 328–330°C.

Although the DSC curve for cell II has a different shape in comparison with cell I, the peak minimum of the second exotherm is situated at the higher temperature of 349°C instead at 328°C. The DSC curve of cell IV has the same shape as that of cell I: the endothermic peak in the temperature range 59–195°C and the exothermic peak split into two peaks with its peak minimum, respectively, at 328–348°C.

The first peak that is endothermic may be due to the evaporation of sorbed moisture and to a dehydration process involving the splitting off of an hydroxyl 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 and to the cleavage of glycosyl units to form low molecular weight sugar derivatives.

DSC of sugar cane and loaded sugar cane shows that the filler has an effect on the course of thermal degradation of cellulose. The thermal stability of this one is higher than that of cell I. Wood is more

Table VII Peak Temperature in the DSC Thermograms for Cells I, II, and IV

	Endotherm (°C)				Exotherm (°C)				
Sample	T_i[a]	T_m[b]	T_f[c]	Enthalpy (J/g)	T_i[a]	T_m[b]	T_f[c]	Enthalpy (J/g)	T_g (°C)
Cell I	52.47	120.53	190.12	−195.753	229.00	327.76 329.13	329.69	487.218	244.36
Cell II	36.89	99.52	157.53	−182.723	245.80	349.19	341.66	280.871	245.43
Cell IV	58.76	123.75	195.05	−162.764	268.75	328.00 347.93	331.93	377.281	244.01

[a] The initial temperature of decomposition of a sample.
[b] The minimum or maximum temperature of the peak.
[c] The final temperature of decomposition of a sample.

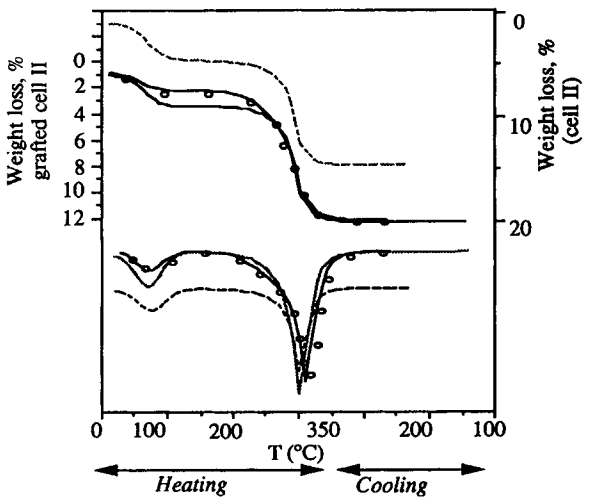

Figure 7 TGA and DTGA curves of cell II grafted with PMMA): (.....) cell II; (———) Ref. 2; (⁀⁀⁀⁀) Ref. 7. Heating rate = 5°C/min. T(°C): 20–300–20.

stable than is bagasse. The same result has been observed by thermogravimetry when the weight loss is less than 10%. Therefore, the three different samples have the following order of stability before dehydration:

$$\text{cell IV} > \text{cell II} > \text{cell I}.$$

After losing between 5 and 10% of their weight corresponding to the water content, wood becomes more stable than is bagasse.

By thermogravimetric analysis, the thermal stability order appears different. Wood pulp is more stable than is the loaded bagasse since the final temperature of dehydration determined by DSC is higher than the one found by TGA. The true initial temperature of pyrolysis is given by DSC.

Therefore, we can say that in the case of DSC all the water has been eliminated (the free and the bounded water). In the case of thermogravimetry, the dehydration is not complete: The bounded water remains in the sample of cellulose. It is eliminated at the same time as the pyrolysis of the cellulose.

Cellulose II Grafted with PMMA

Thermogravimetric Analysis. Four samples containing different percentages of PMMA were prepared and they have the following references: 23.7% (2), 34.6% (3), 36.5% (4) and 56.4% (7).

Figure 7 shows the dynamic TGA and DTGA curves of pulp of sugar cane loaded with $CaCO_3$ and its grafted copolymers with PMMA (refs. 2 and 7). Table VIII gives the thermal analytical data for cell II grafted with PMMA at different grafting yields.

The graft copolymerization of PMMA onto cellulose makes the material thermally more stable (after dehydration) than the ungrafted cellulose. As can be seen, the pyrolysis of cellulose grafted with PMMA samples takes place in two steps: The first one is in the temperature range 29–138°C and corresponds to the phenomenon of dehydration; the second one from 180 to 300°C (depending on the grafting yield) is attributed to the degradation of the glycosyl units.

The PMMA decomposes in the same range of temperature. The graft copolymers contain up to 4% water. The decomposition reaction for the grafted cellulose begins at a higher temperature with 23.7% graft than for the other grafted and ungrafted celluloses. The decomposition temperature (T_D) for

Table VIII Thermal Analytical Data of Grafted Cell II, Wood, and Grafted Wood

			Dehydration					Pyrolysis				
Sample	Grafting Yield (%)	Ref.	T_i (°C)	T_m (°C)	δm (%)	T_f (°C)	δm (%)	T_i (°C)	T_m (°C)	δm (%)	T_f (°C)	δm (%)
Cell II	0.0	1	30.87	76.53	−3.331	152.17	−3.727	183.40	299.00	−10.319	242.03	−9.527
Cell II-grafted PMMA	23.7	2	30.73	71.77	−2.260	137.20	−2.523	188.90	298.27	−9.160	187.80	−8.928
	34.6	3	31.37	72.20	−1.977	137.97	−2.269	186.27	299.87	−8.206	215.43	−7.557
	36.5	4	31.20	70.40	−1.876	134.57	−2.228	184.80	299.13	−7.975	235.37	−6.983
	56.4	7	29.60	66.23	−1.204	130.93	−1.458	184.93	294.83	−9.814	228.57	−9.779
Cell IV	0.0	—	30.73	76.83	−2.814	139.80	−3.026	175.40	295.50	−10.790	224.63	−11.184
Cell IV-*g*-PMMA	70.0	—	36.87	91.77	−1.134	162.13	−1.134	293.43	306.13	−5.293	206.87	−4.852

Table IX Temperature of Decomposition at Different Weight Losses of Cellulose and Cellulose Grafted with PMMA at Different Grafting Yield

Sample	Ref.	Temperature of Decomposition (°C) at Weight Loss of										
		1%	3%	6%	9%	13%	18%	19%	21%	23%	27%	28%
Cell II	1	56.8	75.3	110.8	225.6	284.7	—	301.0	299.7	293.9	129.8	—
Cell II-*g*-PMMA	7	75.3	122.0	259.7	280.7	297.5	—	280.9	257.2	—	—	—
	4	66.3	92.8	259.6	289.2	300.9	—	174.4	—	—	—	—
	3	66.0	92.5	259.7	289.2	300.9	—	257.2	—	—	—	—
	2	61.5	84.1	251.4	280.7	296.8	—	286.4	273.1	94.0	—	—
Cell IV	—	91.0	119.5	254.8	291.0	300.1	306.2	—	—	—	—	212.3
Cell IV-*g*-PMMA	—	110.5	245.3	290.7	299.6	301.5	204.5	—	—	—	—	—

cellulose grafted with PMMA and ungrafted cellulose is shown in Table IX. Comparing T_D at different weight losses, the stability of each cellulose sample differs.

T_D values at 1–18% weight losses are higher for the grafted samples. When 19% weight loss is reached, T_D are higher for the ungrafted cellulose.

Figure 8 shows the temperature dependence of the degree of conversion for the grafted samples. When the weight loss reaches 9% and 13%, the grafted samples with 36.5 and 34.6% of PMMA have the same stability. The same observation is valid for 56.4 and 23.7% of PMMA grafting. At 19% weight loss, the grafted sample become less stable than is the ungrafted sample.

In conclusion, we can say that at different degrees of conversion, T_D will vary and differ from the grafted to the ungrafted sample. The cellulose grafted with PMMA has a higher stability than that of ungrafted cellulose. Beyond 18% weight loss, the ungrafted cellulose became the more stable.

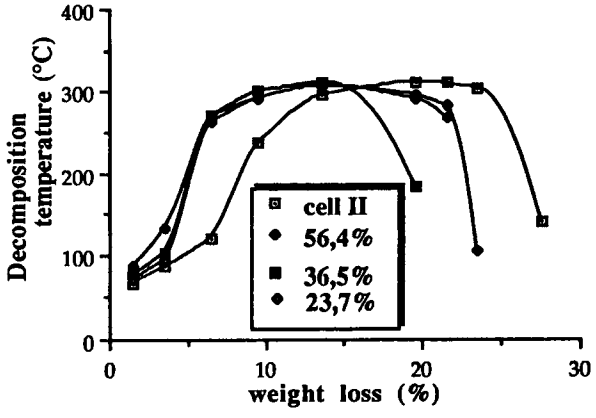

Figure 8 Temperature dependence of the degree of conversion for the pulp II grafted with PMMA at different levels of grafting.

Differential Scanning Calorimetry Analysis. Seven samples containing different percentages of PMMA were prepared and they have the following references: 23.7% (2), 34.6% (3), 36.5% (4), 45.9% (5), 46.25% (6), 56.4% (7), and 62.3% (8).

The DSC curves of the graft copolymers of cell II-grafted PMMA, having different levels of grafting, show two peaks; one endo- and the other exothermic. (For an example, see Fig. 9.) Table X shows the peak temperatures in the DSC thermograms for cell II and cell II-grafted PMMA. The first peak (endotherm) is in the temperature range 55–187°C, and the second one (exotherm), between 274 and 349°C. The temperature of the peak minimum is roughly similar for all samples. The graft copolymers have

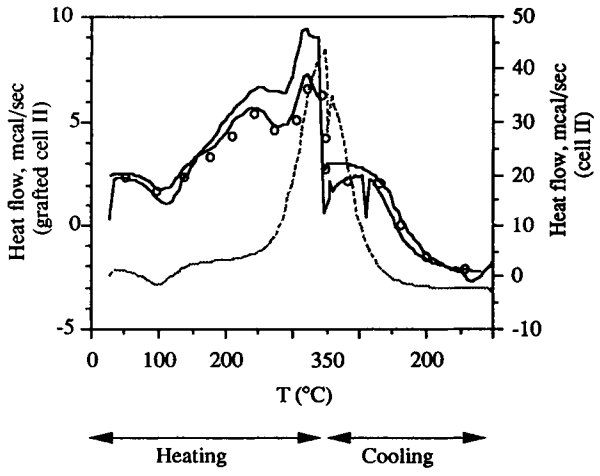

Figure 9 DSC thermograms of the grafted cell II grafted with PMMA: (.....) cell II; (———) 23.7%; (‾OOO‾) 62.30%. Heating rate = 3°C/min. T(°C): 25–350–25.

Table X Peak Temperature in the DSC Thermograms of the Grafted Cellulose II and Wood

Sample	Ref.	Endotherm (°C) T_i	T_m	T_f	ΔH (J/g)	Exotherm I (°C) T_i	T_m	T_f	ΔH (J/g)	Exotherm II (°C) T_i	T_m	T_f	ΔH (J/g)	T_g (°C)
Cell II	1	36.89	99.52	157.53	−182.723	245.80	349.19	341.66	280.871	—	—	—	—	245.43
Cell-*g*-PMMA	2	62.65	121.96	171.40	−97.461	298.34	327.74	336.84	13.746	—	—	—	—	200.49
	3	64.40	120.55	182.73	−85.313	293.75	324.52 348.01	342.48	223.746	—	—	—	—	196.58
	4	60.04	121.66	186.24	−85.632	292.61	325.76	344.94	34.320	—	—	—	—	185.81
	5	56.60	110.70	167.19	−71.943	285.90	324.51 348.34	344.69	206.888	—	—	—	—	181.50
	6	55.53	107.05	161.29	−96.594	286.89	329.65	349.16	13.405	—	—	—	—	187.10
	7	74.35	128.27	182.34	−79.984	269.97	348.71	342.47	266.741	—	—	—	—	196.86
	8	64.62	112.84	162.15	−56.960	273.99	327.84	349.08	28.760	—	—	—	—	182.33
Cell IV	—	58.76	123.75	195.05	−162.764	268.75	328.30 347.65	331.93	337.281	—	—	—	—	244.01
Cell IV-*g*-PMMA	—	70.33	112.96	176.86	−53.666	279.90	323.68	348.59	98.573	—	—	—	—	146.70
Cell IV-*g*-PAN	—	61.34	106.09	158.48	−46.990	203.46	284.08	298.91	29.115	323.12	338.51	349.20	19.039	175.63

an initial temperature of decomposition higher than that of the ungrafted sample. This indicates that the graft copolymers have higher thermostability than the ungrafted cell II. The DSC studies indicate that the thermal degradation of the grafted cell II takes place via two exothermic processes. This is observed for samples containing 34.6 and 45.9% PMMA. In the other grafted polymers, the two peaks were superimposed into a large one. In the case of the grafted sample, a shoulder is observed just before the exothermic peak. These shoulders are not present either in samples 5 and 6 or in the ungrafted sample. Locating the initial temperature (T_i) and the final temperature (T_f) of decomposition in the endothermic peak of the 7, 4, 3 and 2 grafted samples in Table IX of the thermogravimetric analysis, we deduce that the latter contain up to 6% of water.

From the above results, it can be concluded that two mechanisms are involved in the pyrolysis of grafted cellulose in the temperature range 269–348°C. The shoulder observed in the case of some grafted samples of cell II shows that there is probably a change in the mechanism of the process of degradation. Our study shows that the thermostability of cell II grafted with PMMA is higher than that of the ungrafted cell II.

The glass transition temperature of the copolymers is expected to follow the Fox relation[18]:

$$T_g = aT_{g_1} + bT_{g_2}$$

where a is the mole fraction of cellulose in the sample, and b, the mole fraction of PMMA in the sample; T_{g_1}, the glass transition temperature of ungrafted cellulose = 245.4°C for cell II; T_{g_2}, the glass transition temperature of the grafted polymer = 105°C for PMMA; and T_g is the glass transition temperature of the cellulose grafted with PMMA sample.

Indeed, the series of grafted copolymers verified this relation, as is shown in Figure 10, where the experimental T_g is plotted vs. the calculated T_g. For the seven samples, a is equal, respectively, to 0.731

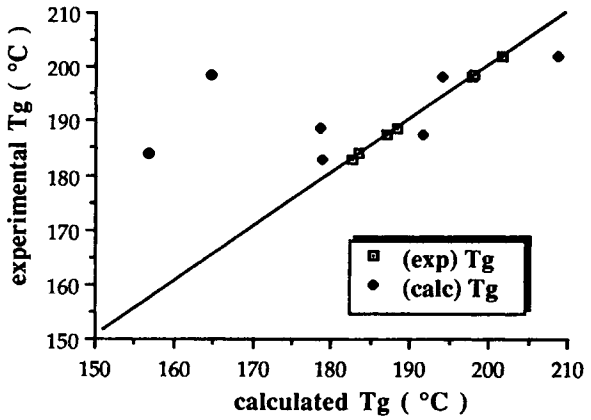

Figure 10 Correlation between the experimental and theoretical glass transition temperature of the cellulosic graft copolymers.

(2), 0.626 (3), 0.608 (4), 0.518 (5), 0.515 (6), 0.418 (7), and 0.361 (8). The discrepancy observed for samples with references 6 and 7 can be attributed to the high ratio of grafting and to inhomogeneous grafting.

Grafted Wood

Thermogravimetry Analysis. Figure 11 shows dynamic TGA and DTGA curves of wood grafted with PMMA. Table VIII gives the initial, maximum and final temperatures of decomposition for dehydration and pyrolysis. The grafted sample decomposed at a temperature higher than that of the ungrafted wood. The maximum pyrolysis is reached at 305–306°C. The grafted sample is more stable than is wood. A shoulder is observed in the range of temperature 208.90–293.43°C in the case of some grafted samples.

Table IX and Figure 12 show the decomposition temperature (T_D) at different weight losses (degree of conversion). From 1 to 13% of its weight loss, the grafted cell IV remains more stable than does the cell IV. Over 18%, cell IV becomes more stable. The presence of PMMA chains in the vicinity of the cellulosic chains modifies the cellulosic structure. When the grafting reaches a certain level, the interchain bondings become weaker and the stability decreases.

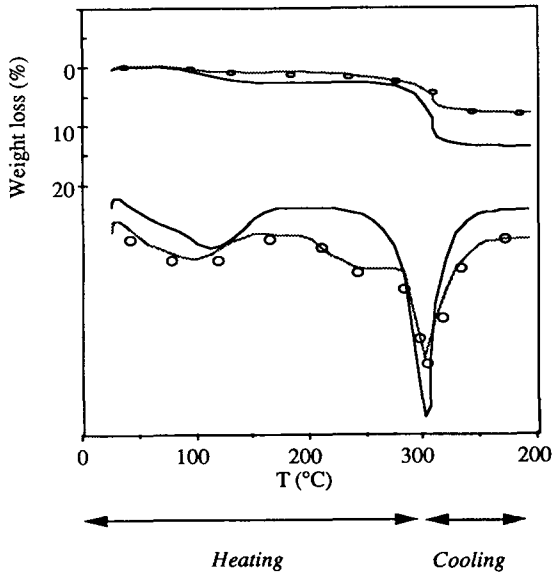

Figure 11 TGA and DTGA curves of ungrafted and grafted wood: (———) ungrafted wood; (‾ooo‾) grafted wood. Heating rate = 10°C/min. T(°C): 20–300–20.

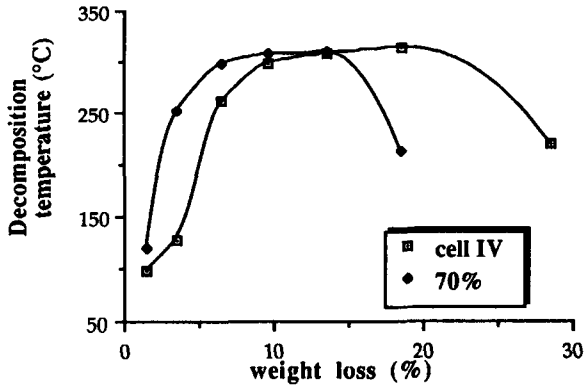

Figure 12 Temperature dependence of the degree of conversion for ungrafted and grafted wood.

Differential Scanning Calorimetry Analysis. The DSC thermograms of wood grafted with 70 and 43%, respectively for MMA and AN show two peaks (see Fig. 13). The peak temperatures of the grafted and ungrafted samples are given in Table X.

In the case of cell IV grafted with PMMA, the peak is in the temperature range of 280°C with a minimum at 324°C. We observe a large shoulder before this exothermic peak. The temperature of decomposition of cell IV grafted with PMMA is higher than that of the ungrafted one and of the cell IV grafted with PAN. The thermal stability of wood grafted with MMA is higher than that of ungrafted wood. This stability remains after dehydration of 2–6% of water. In the case of cellulose grafted with

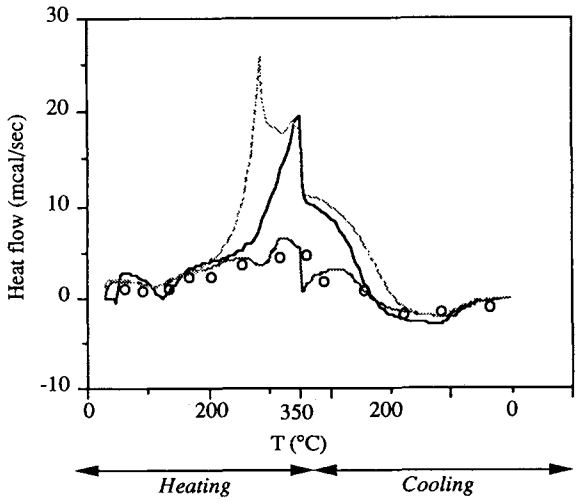

Figure 13 DSC thermograms: (———) cell IV; (‾ooo‾) cell IV grafted with PMMA, (. . . . .) cell IV grafted with PAN. Heating rate = 3°C/min. T(°C): 25–350–25 (°C).

PAN, the decomposition takes place via three peaks, indicating that the decomposition reaction of the graft copolymer is quite complicated. The grafted copolymer with PAN is less stable than is the ungrafted sample after dehydration.

In conclusion, our study shows that the thermostability of cell II grafted with PMMA is higher than that of the ungrafted cell II. The same observation is valid for the grafted dehydrated wood grafted with PMMA. But it is not the case for the wood grafted with PAN. The exothermic peaks observed in the DSC study show that two or more mechanisms are involved probably in the pyrolysis of cellulose and cellulose-grafted copolymers, indicating that the degradation mechanism is complex.

IV. CONCLUSION

Differential scanning calorimetry and thermogravimetric analysis of the pulp of bagasse showed that the $CaCO_3$ filler has a large effect on the course of the thermal decomposition of cellulose and enhances the thermal stability of the pulp of bagasse. The pulp of wood remains more stable than does the pulp of bagasse. The thermostability of cellulose II grafted with PMMA is higher than that of the initial cellulose. The same observation is noted in the case of wood grafted with PMMA. On the contrary, the grafted copolymer with PAN has a lower thermal stability than that of ungrafted wood. The highest stability is observed in the case of the grafted cell II with a level of grafting of 23.7%. The DSC studies indicate that the thermal decomposition of the pulp of bagasse and wood takes place via an exothermic process with a minimum of two peaks. This observation remains valid in the case of the copolymer with a level of grafting of 34.6 and 45.9%. The loaded ungrafted bagasse shows a large exothermic peak. The DSC of wood grafted with PAN shows that the decomposition takes place via two exothermic processes. In some grafted samples, a shoulder is observed just before the exothermic peak, indicating that the decomposition reaction is quite complex.

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