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Modified woodflour as thermoset fillers II. Thermal degradation of woodflours and composites

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Abstract

Composites made from an unsaturated polyester/styrene thermoset matrix and maleic anhydride esterified woodflour have been prepared and tested. Different degrees of esterification of the wood particles with maleic anhydride (MAN) were obtained by using different times of reaction, which led to materials with varied final properties.

X-ray diffraction studies have been carried out on raw and chemically treated woodflours. The degree of crystallinity of modified woodflours is lower than that of the untreated one and decreases as the MAN content of the samples increases. The thermal degradation of the woodflours, matrix, and derived composites was estimated by thermogravimetry (TG) in nitrogen environment.

Thermogravimetry was shown to be sensitive enough to detect differences between woodflour samples with different treatments and degrees of esterification and between composites with different woodflour contents.

Keywords: Woodflour; Composites; Chemical treatment; Thermal degradation; X-ray diffraction

1. Introduction

Polymer degradation can occur due to many factors: heat, 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 of material occur.

Many methods have been used to modify polymers in order to obtain different properties. The present applications of wood filled composites (automobile and decorative panels, insulation systems, packaging) do not include the use of these materials at high temperatures. However, they are exposed to elevated temperature in the processing step (curing reaction in the case of thermoset matrices, mixture with a melt polymer in the case of thermoplastic matrices). Woodflour begins to degrade at relatively low temperature when compared to inorganic fillers. Decomposition of wood components, such as cellulose and lignin creates voids inside the composite, causing a reduction of the mechanical properties [1].

In wood particles, chemical modification is mainly achieved through the reaction of the hydroxyl groups present in the material [2]. In the present work, woodflour (WF) modification was performed by esterification with maleic anhydride (MAN), as described

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in previous paper [3]. The crystallinity of the woodflours and the thermal degradation of WF and related composites can also be affected by the chemical modification. To determine the degree of crystallinity of the different woodflour samples X-ray diffraction was used.

The thermostability of modified woodflours, unsaturated polyester resin and the resulting composites was analyzed by thermogravimetry (TG) in nitrogen. These results were useful to understand changes in the properties of the raw materials due to heating during curing (i.e. maximum temperature reached: 150°C) that might affect the final properties of the composite. Results of the thermogravimetric analysis demonstrate that the technique can also be used with characterization purposes, since they allow to identify differences in degree of esterification of the woodflour or in the woodflour content of the composites.

2. Experimental

2.1. Materials

Specimens of neat cellulose were obtained from ashless filter paper, and neat lignin was gently provided by Granit (Switzerland).

The matrix was an unsaturated polyester (UPE) based on bisphenol A-fumarate (RQ 426, Perlinac S.A., Argentina), crosslinked with styrene in a 60:40 weight proportion with no additives. The initiator was benzoyl peroxide (Lucidol 0.75, Akzo Chemical S.A.), 1.5 wt.% with respect to the total reactive mixture.

Woodflour from *Eucalyptus Saligna* was selected as reinforcing filler because of its availability and wide use in Argentina. Only particles that pass through a sieve of mesh 250 (Tyler series) were used in this study. Thus the maximum particle average diameter was 57 μm.

Woodflour was dried at 70°C for 24 h in a vacuum oven, until constant weight is achieved [3] and part of it was treated with an aqueous solution of NaOH (10 wt.%). The filler was immersed in the solution during 1.5 h at room temperature (mercerized) and then washed several times with distilled water, then with a mixture of water–ethanol (50:50) and finally with ethanol.

Part of the NaOH-treated woodflour was immersed in a 0.6 N solution of MAN in xylene and then heated at reflux temperature (140°C) during 4, 7 or 24 h (depending on the desired reaction level). Then, the esterified wood particles were separated from the xylene solution and intensively washed with distilled water in order to eliminate the unreacted anhydride. Finally, the woodflour was dried at 70°C under vacuum until constant weight was achieved.

2.2. Compounding and molding

Filler and resin were mixed in a Brabender type mixer (volume capacity 50 cm^3) for about 1 h. The paste was filled in a metal mold (145 mm of diameter and about 3 mm of thickness), which was left open during 2 h at 50°C for degassing. Then, the mold was closed and the temperature was increased to 80°C. The reaction was carried out under pressure (3.8 MPa) during 1.5 h. After that time, it was postcured in an oven for 2 h at 150°C.

Samples of neat resin were obtained by pouring the reactive mixture into a glass plate mold of 2.4 mm thickness. Degassing was performed for 1 day at room temperature, followed by the same curing cycle mentioned above.

Three different types of composites were prepared:

1. composites made from untreated woodflour (WF),
2. composites made from mercerized woodflour (NaOH),
3. composites made from MAN-treated woodflour.

In all cases the weight percentage of woodflour was indicated between brackets, i.e. WF (40) indicates a composite containing 40 wt.% of untreated woodflour and 60 wt.% of resin. The degree of esterification of the woodflour was indicated before the word MAN, i.e. 10 MAN (40) indicates a composite made with 40 wt.% of woodflour treated with MAN with a weight gain of 10 g MAN/100 g neat woodflour.

2.3. Methods

The degree of crystallinity of the different woodflours was calculated from X-ray diffractograms recorded from a Philips X-ray diffractometer model PW 1830 with Ni-filtered Cu Kα radiation at 40 kV

and 30 mA. An area method was utilized to evaluate the percentage of crystallinity of the samples:

$$\text{Cryst}\,(\%) = \frac{A_{\text{cryst}} \times 100}{A_{\text{total}}}$$

where cryst (%) is the percentage of crystallinity, A_{cryst} the area from the (0 0 2) plane, peak at $2\theta = 22.6°$ and from the (1 0 1) and the $(1\,0\,\bar{1})$ plane, peak at 13–18°, and A_{total} is the area below the whole region, as shown in detail in Fig. 1. The position of the peaks correspond to those found in native cellulose I diffractograms [4].

Differential scanning calorimetry runs were performed on a Shimadzu DSC-50 at a heating rate of 10°C/min under nitrogen atmosphere.

Thermogravimetric tests were performed using a Seiko Instruments SII Exstar 6000 thermogravimetric analyzer (gently provided by University of Perugia, Italy). The measurements were carried out in a nitrogen atmosphere from room temperature to 500°C at a heating rate of 10°C/min.

3. Results and discussion

3.1. Woodflour

3.1.1. Crystallinity

Wood is a composite material consisting of three major polymers: cellulose, hemicellulose and lignin, which serve as reinforcement and matrix, respectively. It also contains extractives (extraneous components), which are usually low molecular weight, extracellular compounds.

Daniel [5] have reported that previous studies on plant cellulose by means of IR spectroscopy and X-ray diffraction studies indicated that a chief portion of cellulose is arranged in crystalline micelles or crystallites, with interspersed amorphous regions of low degree of order. Native cellulose has a rigid structure, while the rest of the components are amorphous materials accessible to water molecules [6].

In Fig. 2, the X-ray diffraction curves for untreated, NaOH- and MAN-treated woodflours are shown. It can be seen that in all samples the cellulose is present in the crystallographic form I. All spectra show the 22.6° (2θ) reflection and the two broad and unresolved reflections in the range from 13° to 18° (2θ), which have been assigned to the (0 0 2) and the (1 0 1) and $(1\,0\,\bar{1})$ crystallographic planes of cellulose I, respectively [4].

Published studies on native celluloses indicate lattice I can be converted irreversibly to type II [7,8] when celluloses are soaked in aq. NaOH solution

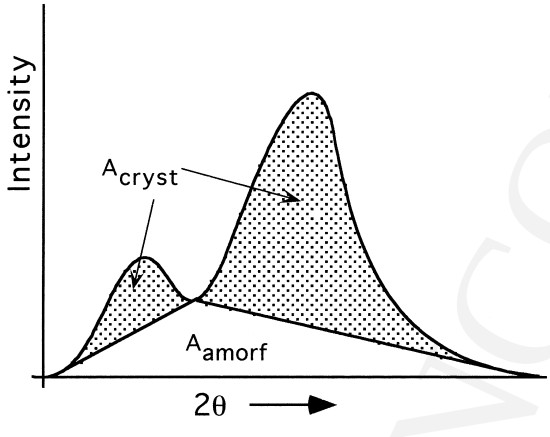

Fig. 1. Typical diffractometer trace of wood used in calculating the degree of crystallinity by the area method.

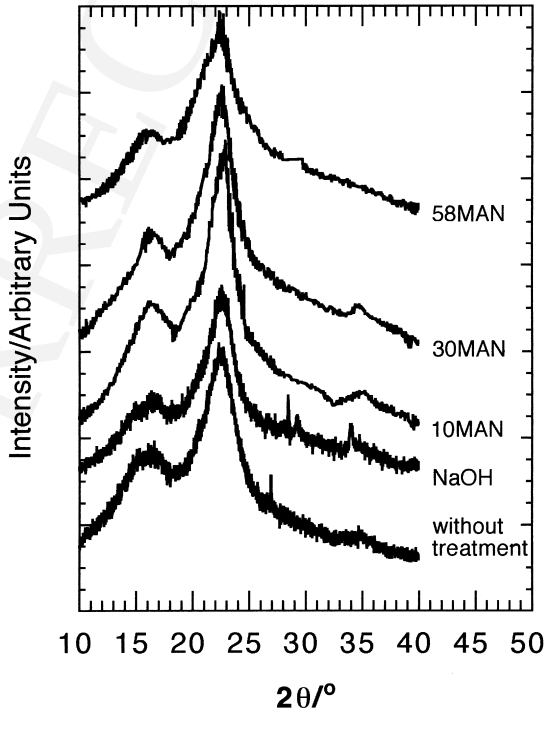

Fig. 2. X-ray diffraction patterns of untreated, mercerized and MAN-treated woodflours.

(mercerization process). However, similar studies on woods or woodmeals showed that no conversion takes place due to strong alkali treatments and in some cases only partial decrystallization occurs [8,9]. Mannam [10] working on the alkali treatment of jute (12–14% lignin) showed that alkali treatments cannot swell cellulose I in jute fiber to the extent needed for mercerization, possibly due to the high content of lignin and hemicellulose that surrounds the crystalline cellulose. The present results shown in Fig. 2 indicate that this is the case in this study, where the diffractogram is consistent with type I cellulose for all of the samples and no cellulose conversion has taken place.

The percentage of crystallinity of the different woodflour samples has also been calculated by the area method described before and are shown in Table 1. It can be seen that the alkaline treatment produces an increment on the percentage of crystallinity of the modified sample, while esterification leads to a gradual monotonical decrease on the crystallinity of the sample.

Previous investigations on alkali treatments of rich cellulose fibers, such as cotton or ramie, have shown that the crystallinity of cellulose decreases with this treatment [2,11]. However, lignocellulosic materials of high lignin content have shown a different behavior. Soaking the material in alkali solutions removes mainly hemicellulose with other constituents, such as proteins, organic acids, pectins, fat, wax [12]. It also removes part of the lignin content in wood products and lignocellulosic fibers, which affects the macrostructural level of the material, although not so the microstructure that is involved in the formation of the cellulose crystals [13,14]. Depending on how harsh the treatment is, the removal of amorphous material can be important, such as the 24% mass loss reported by Gauthier et al. [15] for sisal fibers. It has also been reported that the degree of crystallinity increases as the lignin and hemicellulose polymers were removed [16]. Similar results were presented by Ray [17], who also found that as the lignin and hemicellulose were removed the degree of crystallinity of the fibers tended to approach the typical values of ramie or cotton fibers. Moreover, the percentage of cellulose crystallites in jute calculated on the basis of its cellulose content was the same as that in pure cellulose fibers.

Table 1
Percentage of crystallinity of untreated and modified woodflours calculated according to the area method

Sample	Untreated	NaOH	10 MAN	30 MAN	58 MAN
Cryst (%)	44.7	51.8	47.2	46.5	41.1

Taking into account these previous findings, the loss of mass due to the alkaline treatments was investigated. A careful alkaline treatment (as described in Section 2.1) was done on six replicate woodflour samples, previously dried and weighed, and a loss weight of $17.24 \pm 0.9\%$ due to the dissolution of several constituents of the wood was found. Thus, if the crystallinity of the untreated sample is re-calculated with the assumption that all the material lost is amorphous (mainly lignin and hemicellulose), to make it comparable with the crystallinity of the NaOH woodflour (and MAN-treated woodflours), the corrected percentage is 53.9, very close to the value of 51.83 of the alkaline-treated WF. Summarizing, the NaOH treatment essentially removes lignin and hemicellulose from the woodflour, and the crystallinity of the two samples calculated on the same basis is rather unchanged, in agreement with literature results.

On the other hand, chemical grafting reactions can disrupt the regularity of the crystallites. In their work, Shiraishi et al. [9] explained that chemical reaction begins in the amorphous region of the cellulose, since the reagent cannot diffuse into the crystalline region. Thus, it reacts first at the chain ends on the surface of the crystallites. This results in the opening of some of the hydrogen-bonded cellulose chains, producing some new amorphous cellulose and, as the reaction proceed, more amorphous cellulose is formed. Liao et al. [18] and Moharana and Tripathy [19] found a similar behavior for acrylonitrile grafted wood fibers and jute fibers with methyl methacrylate, acrylonitrile and acrylamide, respectively, and reported that the crystallinity of the fibers decrease with an increase in the ratio of grafting.

Summarizing, the series of esterified samples presented in this work show a gradual but clear reduction in the sample crystallinity, in agreement with the above observations.

3.1.2. Thermal stability

As mentioned before, wood is composed mainly by cellulose, hemicelluloses and lignin. Each of the three

major components of the wood has its own characteristic properties with respect to thermal degradation, which are based in polymer composition. However, the microstructure and three-dimensional nature of wood are variables that also play important roles in terms of their effects on combustion behavior. Thus, the individual chemical components of wood behave differently if they are isolated or if they are intimately combined within each single cell of the wood structure [20].

Lignin, specifically the low molecular weight protolignin, degrades first and at slower rate than the other constituents. This is shown in Fig. 3a: the TGA curve indicates that the beginning of the thermal degradation occurs at approximately 180°C, but the rate of degradation is always lower than that of the cellulose (Fig. 3b). This process has been described by Shukry and Girgis [21], who also presented an analysis of the products of the degradation.

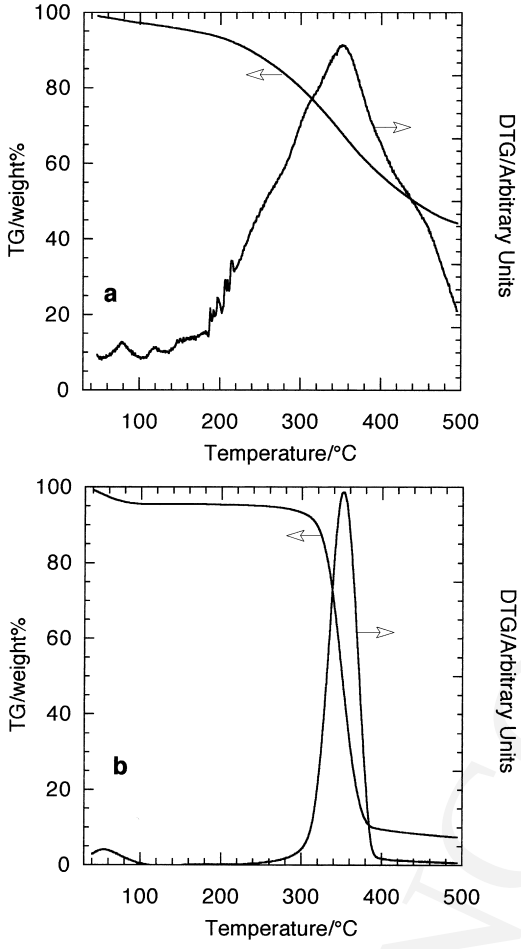

Fig. 3. TG (percentage of weight loss) and DTG (derivative) vs. temperature curves. (a) Lignin, (b) cellulose.

Fig. 3b shows the TG and DTG vs. temperature curves of pure cellulose. It is noticed that the weight loss in the cellulose sample is negligible below 300°C (water desorption being of no concern here). However, above that temperature the cellulose begins to degrade fast and at above 400°C only the residual char is found. Beall [22] has described this process as the loss of hydroxyl groups and the depolymerization of cellulose to anhydroglucose units.

Wood, as a whole material, undergoes a complex degradation scheme, which greatly affects its physical nature. The chemicals produced during pyrolysis of wood are well known, and have been reported in previous works [22–24]. During the thermal decomposition process of wood, small molecules, often flammable or toxic, are eliminated, and eventually a charred mass is left. Except for the loss of absorbed water and volatile oils, the different woodflours are not significantly affected by temperatures up to about 100°C. For untreated woods, noncombustible products, such as carbon dioxide, traces of inorganic compounds, and water vapor are produced between 100 and 200°C. At about 175°C, some components begin to break down chemically: low temperature degradation at low rate occurs in lignin and hemicelluloses.

The mass lost between 300 and 500°C corresponds to the degradation of cellulose as mentioned above and has also been associated to the pyrolitic degradation of lignins involving fragmentation of interunit linkages (releasing monomeric phenols into the vapor phase), decomposition, and condensation of the aromatic rings [22].

Above 450°C, all volatile materials are driven off, and in presence of air the residual char undergoes oxidative reactions [25]. The lignin component contributes to char formation, and the charred layer helps to insulate the material from further thermal degradation.

Figs. 4 and 5 show the results of thermogravimetric tests performed on untreated and treated woodflours. Fig. 4 shows the percentage of weight loss as a function of the temperature (TG) and Fig. 5 shows

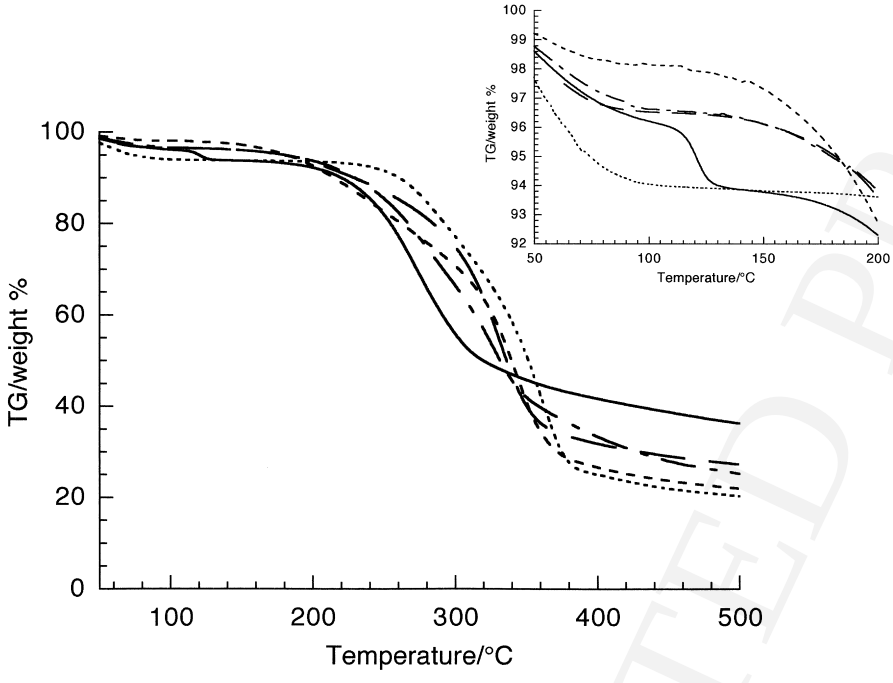

Fig. 4. TG (percentage of weight loss) vs. temperature curves of different woodflours. (· · ·) untreated; (—) NaOH; (— —) 10 MAN; (- - -) 30 MAN; (– - –) 58 MAN.

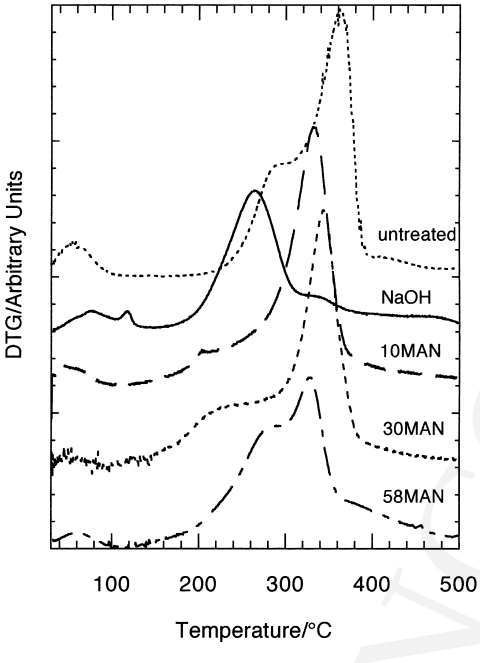

Fig. 5. DTG (derivative) vs. temperature curves of untreated, mercerized and MAN-treated woodflours.

the derivative thermogravimetic curves (DTG). In general, the loss of water is observed below 130°C, and the further thermal degradation appears to take place as a two step process. In particular, it is seen that the water desorption in the alkaline-treated woodflour occurs also in two steps. A small peak is detected at about 120°C in the DTG curve, which has not been assigned to any specific process in the literature. It is proposed that this secondary peak corresponds to the loss of strongly adsorbed water (water held by hydrogen bonds in the wood cell structure). This secondary peak was confirmed by differential scanning calorimetry (DSC): an endothermic peak, with a maxima 134°C, was registered for the humid sample (which occurred with mass loss), and was absent in a second scanning of the sample. Fig. 6 shows the DSC scans of untreated, NaOH and 58% MAN-treated woodflours in order to facilitate the comparison. It can be noticed that untreated and esterified samples lose water in a single step, while the NaOH-treated sample does it in a two step process.

From the thermograms of Figs. 4 and 5, several parameters were evaluated:

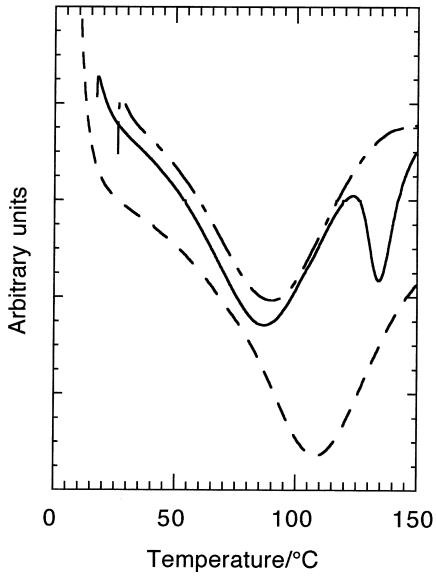

Fig. 6. DSC scans of moist woodflours. (– - –) untreated; (—) mercerized; (- - -) 58 MAN.

1. the ''onset'' of thermal degradation, Td;
2. the amount of desorbed water (as a percentage of mass lost below 130°C);
3. the range of temperatures of the two steps of thermal degradation and the weight lost (as a percentage of the initial mass) in each step;
4. the residual char at 500°C (as a percentage, íd c).

Since the samples presented different amounts of absorbed water and the rate of weight loss is different from sample to sample, Td was taken as the temperature at which the sample suffered a 2% loss of its initial weight, based in the weight of the dry sample, that is after water desorption. The range of temperatures in which degradation occurs was estimated from DTG curves and the weight loss percentage was read from the TG plots. From these results, summarized in Table 2, it can be seen that the ''onset'' of degradation occurs at lower temperatures for all the treated samples, although there is not a clear trend among the esterified woodflours.

The samples of untreated and alkaline-treated woodflours show a similar water content of approximately 6%, although in the last case desorption occurs in two temperature intervals, as was mentioned above. Esterified samples show lower water absorption.

Most of the initial mass is lost during the second step of thermal degradation for all the woodflours, with the exception of the NaOH-treated woodflour. In the case of the esterified samples, the degradation occurs at lower temperatures than in the case of untreated woodflour, while the percentage of mass lost in the first step increases as the degree of MAN grafted to the woodflour increases. Thus, in this temperature range not only low molecular weight lignin and hemicellulose are pyrolized, but part of the ester linkages formed during the esterification reaction are also lost. This behavior has been previously reported by Hassan [26], who claimed that esterified bagasse is less stable than the untreated one because de-esterification reactions occur at low temperatures. The char left at 500°C is in the range of 20–27% for those samples.

Regarding the alkaline-treated woodflour, the main degradation step takes place between 130 and 326°C (44% of mass lost) and this sample presents the highest value of char yield at 500°C (36.5%).

Discussions on the effects of alkaline treatment and grafting reactions on the degradation of different lignocellulosic materials can be found in the literature.

Table 2
Thermal degradation data of untreated and treated woodflour at 10°C/min in nitrogen

Treatment	Td (°C)	Percentage mass loss below 130°C	First step		Second step		Residual char (mass %)
			Temperature (°C)	Percentage mass lost	Temperature (°C)	Percentage mass lost	
Untreated	248	6.6	130–305	18.5	>305	54.4	20.5
NaOH	204	6.4	130–326	44.4	>326	12.7	36.5
10 MAN	188	3.7	130–224	5.3	>224	63.6	27.4
30 MAN	169	2.0	130–269	19.4	>269	56.6	22
58% MAN	188	3.7	130–300	29.8	>300	41.2	25.3

Flaqué and Montserrat [2] analyzed the thermal behavior of mercerized samples and ascribed the process that takes place below 300°C to the loss of water molecules coming from the –OH primary groups. These investigators indicated also that the second step of degradation may be due to the complete loss of –OH groups of monomer units of cellulose and the breakdown of the pyranosic rings. As was observed by Subramaniam and Vasugi [27], the rate at which weight was lost in the whole range of temperature analyzed, was slower for mercerized woodflour. The authors attributed this behavior to the fact that some of the weight of the alkaline-treated woodflour was in the form of inorganic salts, which may have retarded decomposition of cellulose via levoglucosan formation and favored the dehydration process. Subramaniam and Vasugi [27] also reported an increment of the residual char in mercerized cotton with respect to the untreated one, although they did not offer an explanation for this behavior. Daniel [5] stated that impurities, especially inorganic salts, seemed to affect the pyrolysis markedly. Generally, the yield of less volatile materials was reduced as the residue was increased. Similarly, Huang and Li [28] have reported that thermal degradation of cellulosic materials is greatly affected by impurities. Particularly, the initial thermal decomposition temperature is lowered. They have also shown that cotton is less thermally stable after alkaline treatment, the decomposition temperature is shifted about 30°C below the onset of degradation of the untreated cotton. Besides, the same researchers have pointed out that, the lower the molecular weight or the crystallinity, the more readily degradable the cellulosic polymers are, because the percentage of crystallinity decreases as the molecular weight decreases, or in other words, that the molecular weight or crystallinity has a stabilizing effect on the thermal degradation of cellulose. In the present work, it has been shown that the overall crystallinity of the sample is higher for the alkaline-treated sample, although the crystallinity based on nonextractable mass is approximately the same in both cases.

The present study indicates that the overall effect of the alkaline treatment is that of reducing the thermal stability of the woodflour and producing a large char yield. It also shows that the effect of the overall crystallinity of the sample does not play an important role, while the macroscopic changes in the wood structure are probably of major importance in the thermal decomposition of this material.

On the other hand, the esterification reaction affects the crystallinity of the samples and this can have a further effect on the thermal stability of the samples, as it was pointed out before. Flaqué and Montserrat [2] have shown that the free –OH group content is an important factor in the thermal stability of cellulose: for cellulosic grafted copolymers some of the intramolecular dehydratations are not possible because their –OH groups are substituted by grafting, and removal of other products (difficult to eliminate) may occur instead of water elimination. The TG and DTG curves for the MAN-treated woodflours in this study show low temperatures for the ‘‘onset’’ of degradation, which is in agreement with a lower crystallinity of the cellulose fraction of these samples and a low temperature degradation step in which the mass loss is higher than for the untreated woodflour.

Summarizing, thermogravimetric analysis of woodflours indicates that important changes in the wood structure and composition have occurred as a consequence of the chemical modifications of the filler and thus, it could be used as a complementary characterization technique for these type of materials.

4. Composites

4.1. Woodflour treatments

Figs. 7 and 8 show the results of thermogravimetric tests performed in composites containing 40 wt.% of treated and untreated woodflours. Fig. 7 shows the weight loss as a function of temperature, while Fig. 8 displays the derivative TG curves. In both figures, the neat resin thermogram was included in order to facilitate the comparison.

The neat resin is stable below 300°C (only 2.5% of weight loss was detected in this range of temperature). At higher temperatures the sample undergoes a degradation process, which ends above 450°C with almost no residues. The weight loss in the composites begin at lower temperatures than that of the pure matrix, and char yield is larger, about 20% respect to the initial weight, in all cases. DTG curves of the composites show that there is a shift to lower temperatures of the peak that correspond to the main degradation process

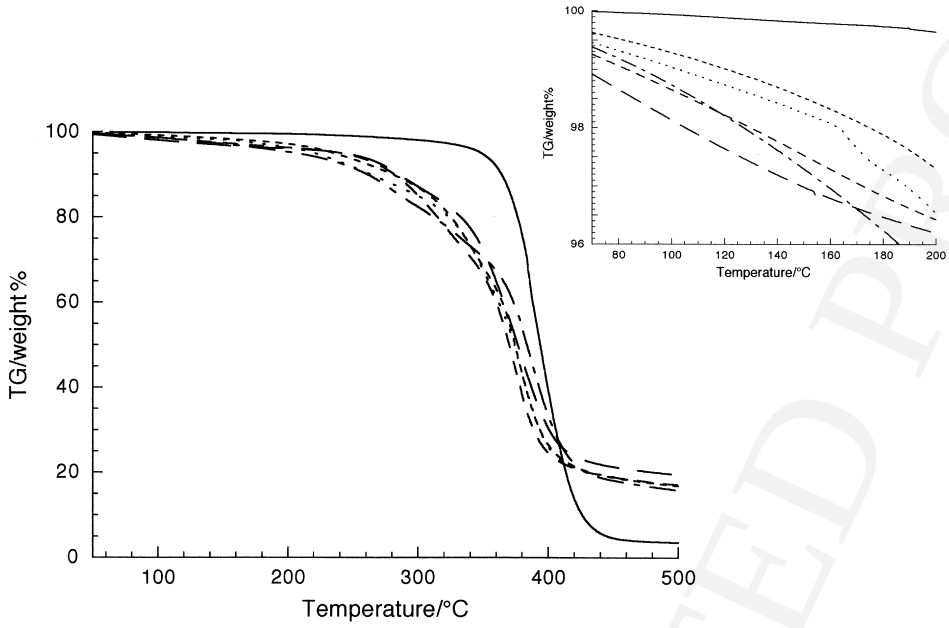

Fig. 7. TG (percentage of weight loss) vs. temperature curves of matrix and composites containing 40% of different woodflours. (—) matrix; (— —) untreated; (– – –) NaOH; (- - -) 10 MAN; (· · ·) 30 MAN; (– - –) 58 MAN.

of the matrix. Besides, when esterified woodflours are used there is an additional degradation stage that occurs at low temperatures (probably the woodflour de-esterification) and there is a shift towards higher temperatures of the peak that corresponds to the degradation process of the WF component of the NaOH-composite.

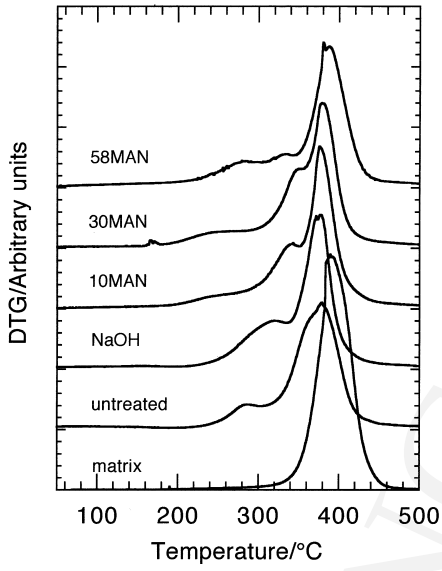

Fig. 8. DTG (derivative) vs. temperature curves of matrix and composites containing 40% of different woodflours.

To investigate a possible interaction between matrix and woodflours in the degradation process of the composites, the DTG curves of some of the composites were calculated from the experimental curves of the matrix and the WFs, which were added taking into account their relative weights in the composites. Fig. 9 shows the comparison between the experimental and calculated DTG curves of the WF (40), 10 MAN (40) and NaOH (40). As anticipated, all the comparisons indicate a shift to lower temperatures of the main decomposition process of the matrix of about 15°C. In the case of WF, the peak at 286°C, which was present in the DTG of the untreated WF, appears at the same temperature. The second peak corresponding to the woodflour, approximately at 360°C, appears overlapped to that of the matrix degradation and shifted to lower temperatures. The DTG curve of the 10 MAN-composite shows the mentioned shift in the matrix peak and a shift towards higher temperatures in the peak of the woodflour degradation. A similar behavior, although much important is shown in the DTG curve of the alkaline-treated woodflour–compo-

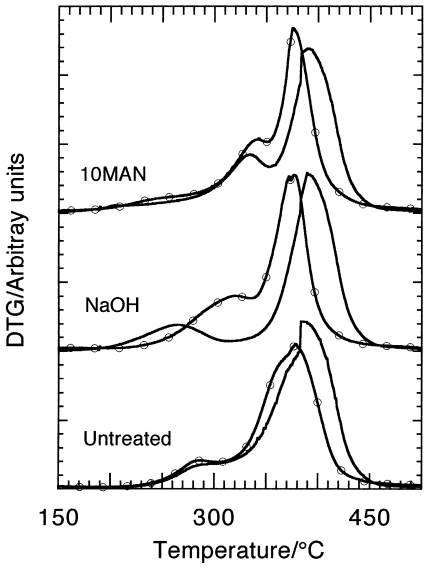

Fig. 9. DTG (derivative) vs. temperature curves of WF (40), NaOH (40) and 10 MAN (40) composites. (⊖) experimental; (—) calculated.

site. The degradation of the WF component is shifted to higher temperatures (about 60°C). Apparently, the presence of the matrix protects the woodflour, delaying its degradation. Besides, the TG curve for this sample (not shown) shows that the calculated amounts of desorbed water and final char yield are in very good agreement with the experimental results. These observations indicate that there is a interaction between the matrix and filler that affects the thermal degradation of the overall material. This interaction is particularly important in the case of the NaOH-composite, where the material is more stable that it could be predicted from the behavior of the individual components.

Table 3 summarizes the thermal degradation behavior of the different composites and the matrix. As in the case of the woodflours, the DTG curves were used to identify the steps of degradation of the composites and the TG curves were used to calculate the mass lost at each stage. Composites made from esterified woodflour show a negligible amount of absorbed water, while composites made from untreated or alkaline-treated woodflours show a gradual decrease of weight below 130°C. Thus, Td for the composites was calculated as the temperature at which a 5% of the initial weight was lost. Using this definition, it can be seen that the ''onset'' of the thermal degradation appears at lower temperatures for the composites (351 and 210°C, for the matrix and the 58 MAN-composites, respectively), following a similar trend to that of the woodflours. The major weight loss occurs in all cases in the last stage of degradation, and it is of 66% in the case of WF and around 50% for the treated woodflour–composites. In the case of the esterified WF–composites, the mass lost in the first degradation step increases with the degree of MAN attached to the woodflour, although the range of temperatures for this degradative process is also broaden.

4.2. Content of woodflour in the composites

Figs. 10 and 11 show the TG and the TG derivative curves vs. temperature for composites made from 10 MAN-treated woodflour at different weight percentages. It can be seen that there are three main steps in the overall degradation process. As the filler content

Table 3
Thermal degradation data of 40 wt.% composites at 10°C/min in nitrogen

Treatment	Td (°C) at 5% loss	First step		Second step		Third step		Residual char (mass %)
		Temperature (°C)	Percentage mass lost	Temperature (°C)	Percentage mass lost	Temperature (°C)	Percentage mass lost	
Matrix	351	–		–		>305	94.3	4.5
Untreated	246	–		160–305	10.4	>305	66.4	20
NaOH	244	–		160–335	25.1	>335	55.1	17.1
10 MAN	238	160–277	7.7	277–352	23.1	>352	50.5	17.1
30 MAN	223	160–280	10.1	280–356	24.2	>356	46.6	17.1
58 MAN	210	160–305	15.3	305–344	9.4	>344	56.3	16.0

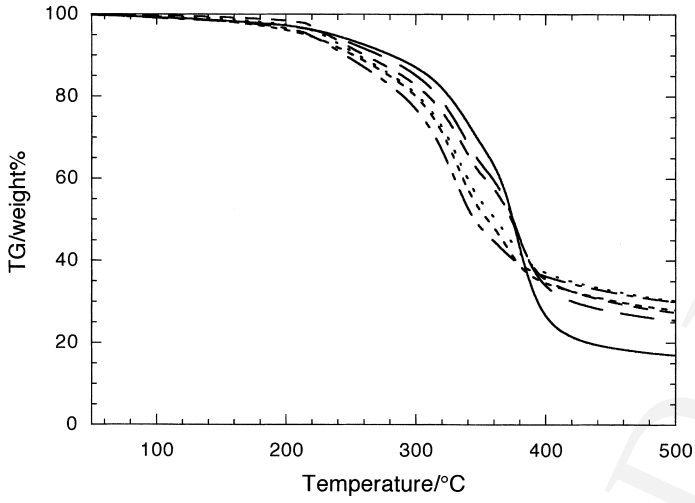

Fig. 10. TG (percentage of weight loss) vs. temperature curves of composites containing different weight percentages of 10 MAN-treated woodflour. (—) 40%; (— —) 50%; (– – –) 60%; (- - -) 65%; (· · ·) 70%; (– - –) 75%.

increases, the DTG curves show that the first two stages, that correspond to the WF degradation, become predominant while the high temperature peak (which corresponds to the matrix degradation) is reduced. It is also observed that the percentage of residual char left at 500°C increases with woodflour content (Table 4), as expected. However, the char yields for the composites with high WF contents are even higher than those corresponding to the 10 MAN-treated WF. This behavior has been observed by other authors [29], and it is the result of the insulating effect of the char originated during the pyrolysis of the woodflour that protects the remaining composite from further thermal degradation. Under these conditions the resin produces more char residues than as a neat polymer.

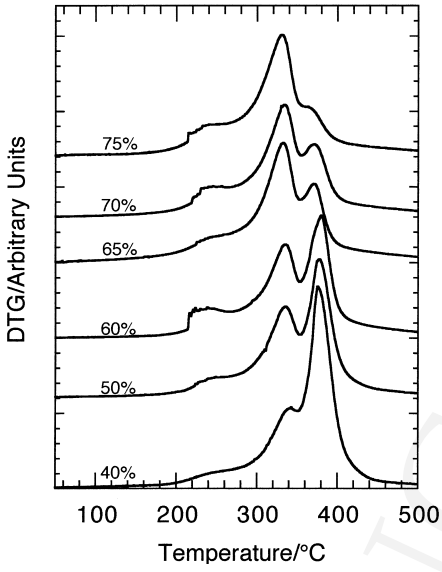

Fig. 11. DTG (derivative) vs. temperature curves of composites containing different weight percentages of 10 MAN-treated woodflour.

Comparisons between calculated and experimental curves (as it was presented for the case of different WF treatments) show important shifts especially in the case of the matrix degradation peak. This peak appears shifted towards lower temperatures (about 25°C in the case of the 75% composite) and the height of the experimental peak is much lower than the calculated one. This indicates that degradation of the matrix begins at lower temperatures, but with a lower rate of decomposition. On the other hand, the first stage of degradation of the WF component begins at higher temperature than the calculated one, but with a higher degradation rate. Finally, the second stage of degrada-

Table 4
Residual char of 10 MAN-composites as a function of the woodflour (wt.%)

Woodflour (wt.%)	40	50	60	65	70	75
Residual char (mass %)	17.1	25.7	27.4	28.2	30.2	30.2

tion of the WF (about 320°C) appears with essentially no temperature shift.

The shifts in the calculated peaks, as well as the char yields measured for the composites are indicating that a strong interaction exists between matrix and fillers, which affects the whole thermal degradation process.

5. Conclusions

Thermogravimetric analysis of woodflours indicates that important changes in the wood structure occur as a consequence of the chemical modifications and percentage of MAN grafting of the woodflour. Thus, it can be potentially a complementary characterization technique for woodflour.

The overall effect of the alkaline treatment is that of reducing the thermal stability of the woodflour and producing a large char yield. This behavior agrees with the effect of the impurities on the pyrolysis of cellulosics materials reported in literature.

The lower thermal stability of the MAN-treated woodflours (when compared with untreated woodflour) is attributed to a lower crystallinity of the cellulose fraction of these samples.

Thermogravimetric studies performed on composites indicated a thermal interaction between fillers and matrix. This was reflected on the shift of the maximum degradation rate peaks of the woodflour towards higher temperatures in the presence of the polymer matrix. Also the peak attributed to the matrix is shifted towards lower temperatures due to the presence of woodflour in the composite. This effect is specially important in the composites prepared with alkali-treated WF.

The thermal degradation of the composites begins at higher temperature than the neat woodflours.

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