Thermochimica Acta, 205 (1992) 39–49
Elsevier Science Publishers B.V., Amsterdam

Characterization of chemically modified chemithermomechanical pulp by thermal analysis. Part 1. Treatment with anhydrides

H.-P. Rensch and B. Riedl

Centre de Recherche en Sciences et Ingénierie des Macromolécules, Département des Sciences du Bois, Faculté de Foresterie et de Géomatique, Université Laval, Sainte-Foy, Quebec G1K 7P4 (Canada)

(Received 25 October 1991)

Abstract

Chemithermomechanical pulp modified by different non-catalytic anhydride treatments was characterized by gravimetric and thermoanalytical methods (thermogravimetry, differential scanning calorimetry). The influence of increasing aliphatic chain length of the anhydride and kind of solvent on the properties of the chemically modified pulp was investigated. TG and DSC measurements were shown to be useful and efficient tools for determination of hydrophilicity and degradation behavior of the modified pulp. A more polar and swelling solvent for the anhydride modification process is shown to be best. The highest reduction in the water uptake was achieved with butyric anhydride compared with propionic and acetic anhydrides. The treatment with acetic anhydride, however, resulted in the highest thermal stability of the modified cellulosic pulp.

INTRODUCTION

Cellulosic fibers used for reinforcement in nonpolar thermoplastics, such as polyethylene, usually have to be modified to enhance compatibility and dispersion between the hydrophilic cellulose fiber and the hydrophobic polymer matrix.

A large variety of modification processes are under investigation [1–4] to change the critical fiber properties which influence the composite performance. In most applications, a reduced hydrophilicity for dimensional stability, enhanced dispersibility and an increased degradation temperature of the fiber is desired. Methods described in the literature are either impregnation treatments or chemical modification processes. The former, such as coating or polymer inclusion, do not result in covalent bonds

---

Correspondence to: B. Riedl, Centre de Recherches en Sciences et Ingénierie des Macromolécules, Département des Sciences du Bois, Faculté de Foresterie et de Géomatique, Université Laval, Sainte-Foy, Québec G1K 7P4, Canada.

0040-6031/92/$05.00

between the reactive parts of the cellulosic material and the modifying agent [5]. The latter build up different types of chemical bonds, depending on the type of chemical reaction which occurs [6-8].

Usually the effect of these fiber surface modifications is characterized indirectly by its influence on the mechanical and thermal properties of the resulting composites [2,7]. But the manufacture of composites is a time and energy consuming process, including a multitude of additional parameters to influence the final composite properties. Often the effects of composite processing overlie the effects of surface modification and lead only to empirical results about the efficiency of the fibre modification. Thermal analysis, on the other hand, enables one to study directly various effects of the fiber modification which decisively influence the composite properties such as the water uptake and degradation behavior [9,10] of the material. Because it is a fast and material saving analytical method, thermal analysis can therefore contribute to a first judgement of the efficiency of a surface and interface modifying process.

In the first part of the following study, cellulosic fibers in the form of chemithermomechanical pulp (CTMP) will be modified with different anhydrides in swelling and non-swelling solvents. The effects of these fiber treatments will be analyzed by gravimetric methods, differential scanning calorimetry (DSC) and thermogravimetry (TG), in this paper. In the second part of the study, to be published later, the effects of different non-catalyzed isocyanate treatments on the same material are studied. Subsequent studies will use spectroscopic methods to examine the influence of these treatments on the fiber surface chemistry and on composite properties.

Treatment with anhydrides

Treatment of cellulosic material with anhydrides is carried out to achieve covalent (ester) bonding with the reactive hydroxyl groups on cellulose, hemicelluloses and lignin. As anhydride treatment of cellulosic material is a single site reaction, the weight gain can directly be converted into units of hydroxyl groups blocked. A disadvantage is the formation of an acid by-product, which results in a loss of 50% of the reaction chemical as well as possible strength losses due to acid hydrolysis of the ester bonding.

The acetylation process is known for good penetration of the wood structure and a high degree of reduction of swelling, combined with improved mechanical properties of the acetylated wood [11,12]. Extensive studies show the influence of acetylation on the antishrink efficiency (ASE), color, density and mechanical properties of acetylated wood [13,14]. For CTMP, the effect of different degrees of acetylation on the reinforcement behavior in polyethylene/polypropylene wood fibre composites was investigated recently by Riedl and coworkers [15]. Best results in terms of mechanical composite properties were achieved at 10 wt% acetylation (in the gas phase) of the CTMP. Acetylation treatment at this level reduced the polarity of the cellulose lignin surface and increased the interaction between the polyolefin and CTMP.

Many of the properties of cellulosic material chemically modified with anhydrides depend on the surface modification method used. The temperature of treatment, time of reaction, and type as well as amount of catalyst play a significant role in the extent of fibre modification and degradation during treatment. Anhydride treatment in general can be done without a catalyst in solution or in the gas phase. Propionic and butyric anhydrides were shown to react at a significantly lower rate with wood than acetic anhydride [13]. Non-catalytic treatment of the pulp will be chosen in the following study in order to avoid surface contaminations, which influence the degradation behavior and impede the spectroscopic characterization of the material.

EXPERIMENTAL

Materials

As cellulosic material, a chemithermomechanical pulp composed of 45% spruce, 45% fir and 10% poplar from Stone Consolidated Inc. Bathurst Div. (Bathurst, New Brunswick, Canada) was used. After defibration and grinding, the pulp was sieved to mesh size 30. For fibre modification, various anhydrides were used which differed only in the length of their aliphatic chain. Acetic anhydride, propionic anhydride, butyric anhydride and the solvents were supplied by Aldrich (ACS grade).

Modification of CTMP with anhydrides

The oven dry CTMP was treated with 2.65 M acetic or propionic anhydride in xylene (as non-swelling agent) and in DMF (as swelling agent) without any catalyst. Treatment with butyric anhydride was done only in DMF as solvent. Prior to the anhydride treatment in DMF, the dry CTMP was soaked with the solvent for 30 minutes to allow swelling of the pulp.

Reaction conditions in xylene: 2 h at 125°C; reaction conditions in DMF: 1 h at 125°C. The chemically treated fibers were repeatedly washed with the pure solvent and part of the fibers was cleaned additionally by water extraction (sample A11), with measurements being made on the two kinds (see Table 1).

Apparatus and operating conditions

For the thermoanalytical studies, a Mettler TA4000 Thermal Analysis System with DSC 20 and TG 50 was used. DSC measurements were carried

TABLE 1

Characterization of modified CTMP by gravimetry and DSC

Sample	Modifying agent	Process conditions	Weight gain [a] (wt%)	Water uptake [b] (wt%)	67% r.h. [c] $\Delta H_{\mathrm{nitrogen}}$
CTMP	–	Untreated	–	9.8	224
AO	–	Xylene, 125°C, 2 h	0.0	10.4	236
A1	Acetic anhydride	2.65 M, xylene, 125°C, 2 h	11.1	5.1	129
A11	Acetic anhydride	A1 + water extraction	7.3	6.1	143
A2	Propionic anhydride	2.65 M, xylene, 125°C, 2 h	0.8	7.9	202
B0	–	DMF, 125°C, 1 h	0.0	11.1	250
B1	Acetic anhydride	2.65 M, DMF, 125°C, 1 h	17.9	5.0	108
B2	Propionic anhydride	2.65 M, DMF, 125°C, 1 h	20.0	3.9	75
B3	Butyric anhydride	2.65 M, DMF, 125°C, 1 h	18.8	3.5	67

[a] Oven dry sample. [b] Difference in weight between oven dry and humidified (67% r.h.) sample. [c] Enthalpy of the endothermic peak of the humid (67% r.h.) sample between 35 and 140°C measured by DSC.

out with 6.5–7.5 mg of CTMP at a heating rate of 20°C min^{-1}. As inert atmosphere, dried nitrogen with a flow rate of 50 ml min^{-1} was used. As oxidizing atmosphere, air was used in order to simulate the later composite processing conditions. To optimize atmospheric interaction, the lids of the aluminum crucibles were perforated. TG measurements were done with the same amount of sample and heating rate. The flow rate of purge gas was 90 ml min^{-1}. For isothermal TG measurements the samples were inserted in the TG cell under a nitrogen flow at 220°C. After their adaptation to the temperature, the purge gas was switched to air prior to the measurement of the isothermal weight loss.

Procedure

Prior to the chemical treatment, the CTMP was dried in an air convection oven (105°C) for 3 days and stored under phosphorus pentoxide for 24 h. The weight change of the dry sample due to the chemical modification was determined gravimetrically.

Water uptake before and after modifying the CTMP was examined by gravimetry, thermogravimetry and differential scanning calorimetry. The samples were used in dry condition (as described above) and after storage in a humidity chamber at 67% r.h. at 20°C for about 7 days until no further weight change took place.

The amount of water uptake was determined as weight loss of the sample between 35 and 140°C by TG and from the enthalpy of the endothermic dehydration peak by DSC. Preliminary studies showed that this endothermic effect was a reversible one, and that its energy change was dependent on the humidity of the sample (Fig. 1).

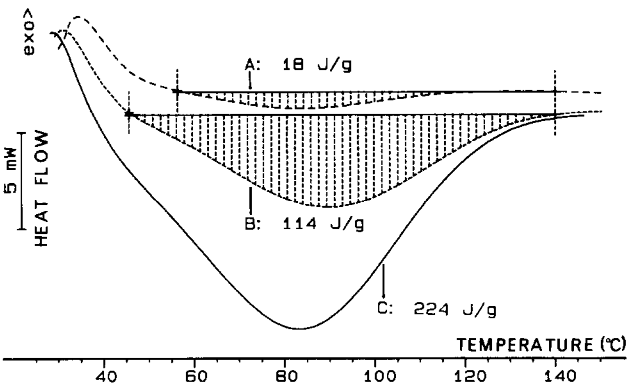

Fig. 1. Changes in heat of dehydration of CTMP exposed to different humidities, measured by DSC at 20°C min^{-1} (A: dry; B: 37% r.h.; C: 67% r.h.).

The enthalpy of the cellulose dehydration was calculated by an approach which used a linear baseline as shown in Fig. 1. This method includes a certain inaccuracy caused by the initial deviation (difference between starting point and stabilized signal), because measurement was started before adaptation of the sample to the conditions of the DSC cell. The immediate measurement of the humidified samples is nevertheless necessary to guarantee that the enthalpy determined by DSC is representative of the water uptake of the conditioned sample.

Since the heat of vaporization of water at its normal boiling point is 38916 J mol^{-1}, or 2263 J g^{-1}, and the weight gain of CTMP exposed to 67% relative humidity is 0.098 g per g sample (Table 1), the estimated heat required for evaporation would be 222 J g^{-1} (2263 J $g^{-1} \times$ 0.098 g per g sample) [16]. The difference between the enthalpy of the humid sample (224 J g^{-1}) and the dry one (18 J g^{-1}) was shown to be 206 J g^{-1} by DSC measurements. This indicates that the energy change measured by DSC is due to the loss of absorbed water. The variation of the results ranges between 7 and 14% (for three samples), because the beginning of the dehydration reaction is near the starting temperature.

DSC measurements were done in a dried nitrogen atmosphere to avoid surface oxidation and to increase the reproducibility of the enthalpy determinations. However, to predict the thermal degradation behavior of the CTMP in the later composite processing, air was used as an oxidizing atmosphere.

RESULTS

Gravimetry

Treatment of CTMP with acetic anhydride (sample A1) and propionic anhydride (sample A2) in xylene results only in the former case in a significant weight increase (11.1 wt%), as can be seen in Table 1. Furthermore, this acetylation process results in a reduction in water uptake of the modified pulp by half. Treatment of CTMP with propionic anhydride in xylene under similiar process conditions results only in a very small weight increase. Water uptake is reduced by one fifth compared with the untreated pulp. On the other hand, the use of DMF as solvent for the anhydride treatment leads to a high increase in weight gain with acetic as well as propionic and butyric anhydrides (Table 1). This correlates with remarkable reductions in water uptake of the modified pulp. Treatment with butyric anhydride yields a modified pulp with a water uptake of 3.5 wt%, compared with 9.8 wt% for the untreated CTMP. In contrast to the results in xylene as solvent, in DMF the water uptake decreases with increasing chain length of the anhydride used for CTMP modification.

Extraction of the acetylated CTMP (xylene as solvent) in distilled water shows a reduction in weight gain from 11.1 to 7.3 wt%, resulting in an increase in water uptake from 5.1 wt% to 6.1 wt% (±0.5 wt%), respectively (Table 1).

Differential scanning calorimetry

As discussed before, the endothermic peak in the temperature range up to 140°C can be used to estimate the amount of absorbed water, i.e. the hydrophilicity of the CTMP. The enthalpy of the dehydration peak of modified CTMP is strongly dependent on the type of anhydride (Fig. 2) as well as on the kind of solvent used for the chemical modification (Table 1). The decrease in enthalpy due to chemical modification of CTMP is always accompanied by a shift in the peak temperature and in the final dehydration temperature to lower values, as can be seen in Fig. 2a and 2b. This indicates that absorbed water is being removed at relatively lower temperatures for the modified CTMP than for the untreated CTMP. As far as the effects of the solvent are concerned, a further reduction in peak and final dehydration temperature takes place if we use the more polar and swelling solvent DMF for acetylation instead of xylene.

Beyond this, DSC experiments show the possibility of detecting the minor changes due to a water extraction of the acetylated CTMP (sample A11). The increase in water uptake determined by gravimetric methods can be observed as an increase in the enthalpy of the dehydration peak in the DSC diagram (Table 1). Simultaneously, the extracted sample shows an increased thermal stability in comparison with the acetylated (A1) and untreated CTMP (Table 2).

TG measurements

Dynamic TG measurements of CTMP modified by anhydride treatment were made under conditions similar to those used for DSC. TG experi-

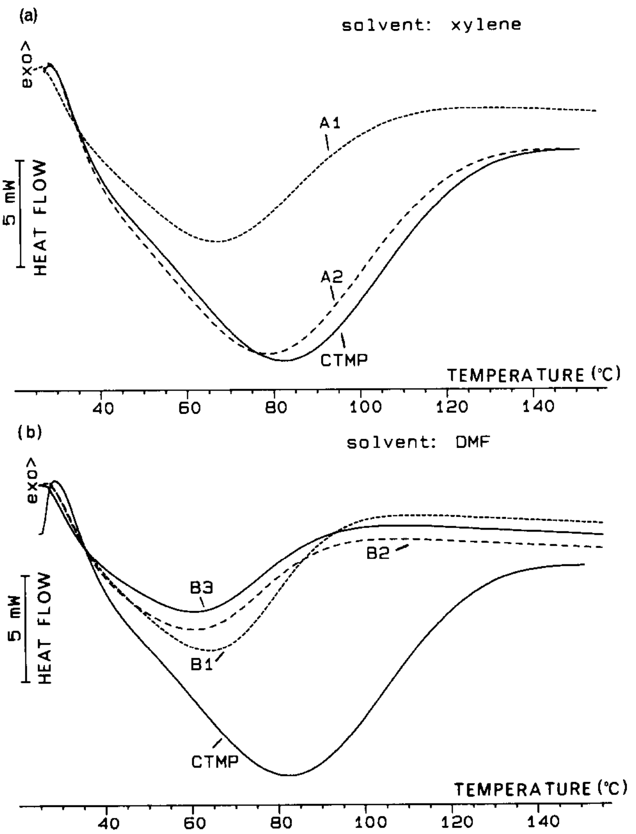

Fig. 2. Influence of anhydride treatment of CTMP (a) in xylene, (b) in DMF, on the water uptake of the humid sample (67% r.h.), determined by DSC (20°C min^{-1}, nitrogen).

TABLE 2

Influence of anhydride treatment of CTMP on thermogravimetric results (dynamic TG in nitrogen at 20°C min^{-1} and isothermal TG in air)

Sample	Dynamic TG				Isothermal TG Weight loss [b] (wt %) at 220°C, 1 h, in air
	Weight loss [a] (wt%)		Peak temperature [a] (°C)		
	40–140°C	180–400°C	40–140°C	180–400°C	
CTMP	8.6	65.5	46.7	349.0	13.9
A1	5.1	69.4	43.9	350.0	15.7
A11	6.2	73.4	43.0	361.0	12.6
A2	7.8	66.8	46.7	348.3	15.6
B0	8.6	66.5	47.6	353.1	14.3
B1	4.6	73.4	43.3	361.7	7.8
B2	3.1	75.8	40.0	363.2	8.9
B3	2.7	76.6	41.0	361.0	10.1

[a] Oven dry sample. [b] Difference in weight between oven dry and humid (67% r.h.) sample.

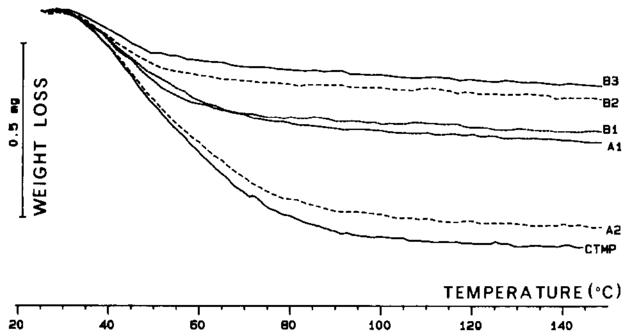

Fig. 3. Weight loss due to water uptake of modified CTMP, determined by TG (20°C min^{-1}, nitrogen).

ments up to 400°C show two steps in weight loss at 35–140°C and 180–400°C for CTMP. The first step can be referred to the water uptake, and the amount of weight loss is dependent on the degree of humidity of the sample. The second step is related to the degradation of the cellulosic material. In Table 2 the weight loss and the peak temperature of the derivative peak (DTG) of the two steps are represented.

Acetylation in xylene and in DMF show similar results in reduction of water uptake, but the former shows a significantly reduced DTG peak temperature for the degradation step. Water extraction of the CTMP acetylated in xylene increases the water uptake slightly but increases also the DTG peak temperature of the degradation step. This indicates a thermally more stable product. Propionic anhydride treatment of CTMP reduces the weight loss due to water uptake more effectively in DMF than in xylene as solvent. In DMF the increase in chain length results in an additional reduction in water uptake. Figure 3 shows a decreasing weight loss in the sequence CTMP > A2 > A1 > B1 > B2 > B3. The decrease in weight loss is accompanied by a shift in peak temperature of the DTG to smaller values (Table 2). Being analogous to the maximum rate of weight change, the change in DTG peak position shows the maximum rate of water desorption shifted to lower temperatures.

Simultaneously, the maximum rate of degradation is shifted to significantly higher temperatures, as can be seen from the peak temperature of the DTG peak in Table 2. Anhydride modified CTMP (samples B1, B2, B3) show a clearly reduced degradation up to 370°C in comparison with untreated CTMP. The comparison of the degradation behavior as shown in Fig. 4 indicates that the anhydride modification in DMF delays the starting temperature of the dynamic degradation of CTMP in nitrogen. This delay in degradation of the modified CTMP could give an important advantage by allowing increased usage and processing temperatures in composite manufacturing. Therefore more detailed isothermal experiments were done

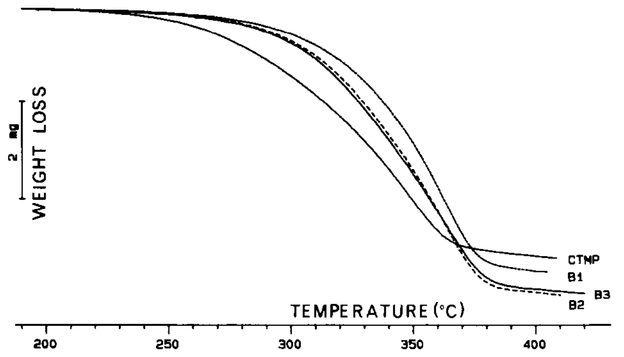

Fig. 4. Weight loss of CTMP modified by anhydrides in DMF (for samples as identified in Table 1), determined by TG (20°C min^{-1}, nitrogen).

at 220°C in air. Figure 5 shows that the isothermal weight loss in air for anhydride treated CTMP in DMF is smaller than for untreated CTMP. But acetylation in xylene does not inhibit the thermal degradation of CTMP: it even slightly increases it. This agrees with results of isothermal DSC experiments (not shown here). Extraction of the acetylated sample in water, however, results in a higher thermal stability, possibly due to removal of the acid.

COMPARISON OF DIFFERENT METHODS USED

DSC measurements give a good correlation between the enthalpy of dehydration and the water uptake of different chemically modified CTMP samples. An advantage in comparison with gravimetric experiments is the small amount of material needed and the speed it affords for such screening experiments. TG experiments provide information about the hydropho-

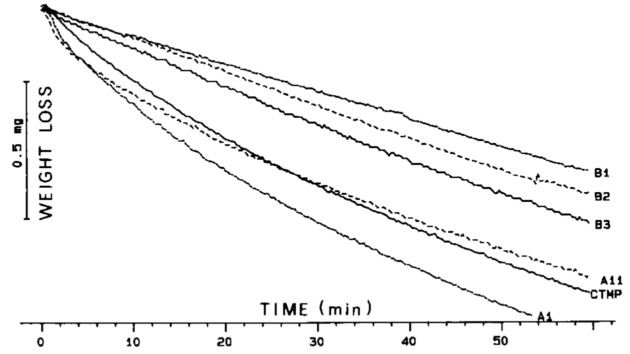

Fig. 5. Isothermal weight loss of anhydride modified CTMP at 220°C in air (for samples as identified in Table 1).

bicity of the modified samples by determination of the weight loss due to the dehydration of the humidified sample. Both methods are independent of the heating rate. A change of purge gas from nitrogen to air causes only minor differences. Comparison of the data gained by gravimetric, DSC and TG measurements (Tables 1 and 2) shows the same tendency for the different modified samples. Differences in the absolute value of the water uptake determined by gravimetry and TG may arise from the loss of humidity during conditioning prior to the TG measurement.

Beyond the determination of the water uptake, TG experiments are useful for rapid characterization of the degradation behavior of the modified pulp. In contrast to the water uptake, such behavior is strongly dependent on the heating rate and the kind of purge gas. Isothermal experiments are therefore more useful.

CONCLUSIONS

Acetylation of cellulose pulp in xylene or DMF achieves a high degree in reduction of water uptake. The use of xylene as solvent leads to a chemically modified material with decreased thermal stability compared to untreated CTMP. A subsequent water extraction increases the water uptake slightly but achieves a higher thermal stability. Anhydrides with increasing chain length show no reaction with CTMP in xylene.

In DMF as solvent, propionic and butyric anhydrides can react with the CTMP more easily and yield a product with a higher reduction in water uptake than is achieved by acetylation. Although the degree of reaction of the CTMP decreases with increasing chain length of the anhydride, the hydrophobicity of the modified CTMP increases.

Dynamic and isothermal TG studies show an enhanced thermal stability of CTMP modified with anhydrides in DMF in comparison with untreated CTMP. This could achieve an important advantage in manufacturing of composites at higher temperatures and will be studied in the future. In contrast to results of wood treatment with propionic and butyric anhydrides in xylene, which show poor reaction [13], treatment of CTMP in presence of a swelling agent like DMF appears to be an interesting method for modifying cellulose pulp properties in order to achieve a less hydrophilic and thermally more stable product.

Thus it is shown that thermoanalytical methods have a high potential for rapid screening of chemical modification techniques of cellulose pulp.

ACKNOWLEDGMENTS

We thank the Natural Sciences and Engineering Council of Canada as well as the Fonds pour la Formation de Chercheurs et l'Aide a la Recherche of Québec (F.C.A.R.) as well as the Centre Québecois de la Valorisation de la Biomasse (C.Q.V.B.) for funding of DSC facilities and Stone Consolidated Inc. Bathurst Division for the supply of cellulose pulp.

REFERENCES

1 R.M. Rowell, American Wood-Preservers' Association, 1975, p. 41.

2 C. Klason and J. Kubat, in L. Salmen (Ed.), Composite Systems from Natural and Synthetic Polymers, Elsevier, 1986, p. 65.

3 H. Dalvag, C. Klason and H.-E. Stromvall, Int. J. Polym. Mater., 11 (1985) 9.

4 R.G. Raj and B.V. Kokta, J. Appl. Polym. Sci., 38 (1989) 1987.

5 A.D. Beshay, B.V. Kokta and C. Daneault, NRCC-IGM Symposium, Composites 84, Proceeding of Papers, 8200-8-1.4, Boucherville (11.1984) 10.0.

6 R.E. Swanson, Tappi, 61(7) (1978) 77.

7 R.G. Raj, B.V. Kokta, G. Grouleau and C. Daneault, Polym. Plast. Technol. Eng., 29 (4) (1990) 339.

8 B.V. Kokta, D. Maldas, C. Daneault and P. Beland, Polymer Composites, 11(2) (1990) 84.

9 C.N. Saika, N.N. Dutta, J.N. Baruah and N.N. Dass, Thermochim. Acta, 168 (1990) 9.

10 B.V. Kokta and J.L. Valade, Tappi, 55(3) (1972) 375.

11 W.A. Dreher, I.S. Goldstein and G.R. Cramer, For. Prod. J., 14 (1964) 66.

12 B.R. Baird, Wood Fiber, 1 (1969) 54.

13 I.S. Goldstein, E.B. Jeroski, A.E. Lund, J.F. Nielson and J.M. Weater, For. Prod. J., 11 (1961) 363.

14 I.P. Clermont and F. Bender, For. Prod. J., 7 (1957) 167.

15 B. Riedl, H. Chtourou and A. Ait-Kadi, Recyclado de Plasticos, Madrid, 1990.

16 M.S. Bertan and B.E. Dale, J. Appl. Polym. Sci., 32 (1986) 4241.