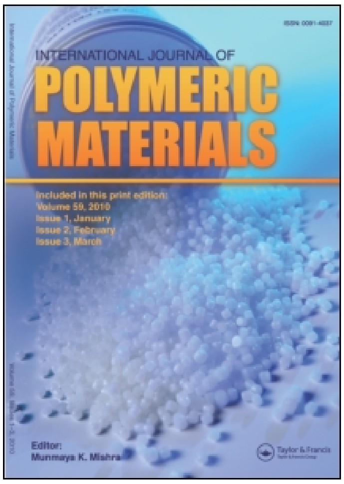

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Benzylcellulose from a Cotton Residue Cellulose: Characterization by Thermal Analyses and Infrared Spectroscopy

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Benzylcellulose from a Cotton Residue Cellulose: Characterization by Thermal Analyses and Infrared Spectroscopy

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Cellulose from a cotton residue was isolated, characterized and used for benzylcellulose preparation. A comparative study was done using a commercial cellulose. IR, DSC and TGA were used to characterize celluloses and benzylcelluloses. Experimental data showed that the cotton residue cellulose has a different thermal behavior compared to other celluloses. On the other hand the infrared spectra are identical. Benzylcelluloses with high substitution degree obtained by reaction of celluloses with benzylchloride, showed very similar thermal behavior, but a little higher thermal stability of the commercial cellulose derivatives was always observed.

Keywords: Cellulose; cotton residue; benzylcellulose; infrared spectroscopy; thermo- gravimetry; differential scanning calorimetry

INTRODUCTION

Cellulose is a particularly important natural polymer, on one hand it is the most abundant material produced by photosynthesis and widely used by humans, on the other hand. The chemical structure and availability of

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abundant hydroxyl groups responses for the wide diversity of uses of cellulose (fiber, paper, film, plastic, etc.). The areas of application are very numerous, the annual world consumption is very high (about 150 million ton in 1988 [1] without considering wood consumed as fuel and lumber) and is expected to rise year after year.

There are numerous cellulosic materials obtained as by-products in industrial processes or in crops harvests. Sugar cane bagasse, soybean husk, cotton residues and wheat, corn and other cereal straws are some important examples of this type of materials that frequently constitute sources of environmental contamination.

One of the attempts to find new utilization possibilities of the cited materials is through chemical modification. Thermoplastics obtention from pineapple, rice and/or wood residues by means of benzylation [2, 3] and cyanoethylation [4] were reported. Success was obtained, for example, benzylated wood was found to be easily extruded or molded into different shapes [2].

Some properties of cellulose are improved through benzylation such as elastic recovery, microbiological resistance and becomes a thermoplastic. Benzylcellulose is largely used in lacquers, spindle oils, shoe stiffness, battery cases, etc. [5].

In this work, cellulose was obtained from a cotton industrial residue and used for benzylcellulose preparation. Both, cellulose and benzylcellulose were analyzed through infrared spectroscopy, thermogravimetry and differential scanning calorimetry. For comparison purposes, a commercial Carlo Erba cellulose was also used.

EXPERIMENTAL

The cotton residue used in the study was obtained from a local cotton industry (SANBRA). The composition of this sample was determined using conventional methods [6, 7], and the following results were obtained: cellulose 40%, hemicellulose 23%, Klason lignin 22%, extractives 15% and ash $< 0.01\%$. For cellulose isolation the cotton residue was first milled and treated with NaOH 5% solution at 120°C during 15 min. The remaining lignin and hemicelluloses were extracted with acid solution (HCOOH 88%, HCl 0.3%) in reflux during 1 hour. Finally, the sample was bleached with hypochlorite (2,0–2.5% active chlorine) in acidic conditions (HCl) stirring during 30 min at room temperature. The cellulose obtained was filtered, washed with distilled water and dried at 50°C for 15 hours.

For cellulose characterization, α- and β- cellulose content was determined [6] of the cellulose from cotton residue and of a commercial cellulose (for chromatography from Carlo Erba) for comparison. The original cellulose, α- and β-cellulose were analyzed through infrared spectroscopy (KBr pellets, JASCO IR700), Thermogravimetric Analysis (TGA, SHIMADZU TA-50, nitrogen flow 10 mL/min, 10°C/min) and Differential Scanning Calorimetry (DSC, SHIMADZU DSC 50, heating rate 10°C/min, nitrogen flow 20 mL/min).

Celluloses were used for benzycellulose obtention using the method described in reference 3. Cellulose was activated with concentrated NaOH solution and then reacted with benzylchloride at 105°C. Samples were taken at different reaction times (1–48 hours) and also analyzed by IR, TGA, and DSC.

Apparent activation energy of pyrolysis were calculated from the TGA curves by the method of Broido and Williams [8].

RESULTS AND DISCUSSION

Celluloses

Cellulose obtained from an industrial cotton residue was analyzed and compared with a commercial cellulose (Carlo Erba). α- and β-cellulose content are in Table I and show significative differences.

Infrared spectra of both celluloses and corresponding α- and β-celluloses are in Figures 1 and 2. Some differences are observed between the original celluloses an the α- and β-celluloses: the 1280 cm^{-1} peak is shifted to 1260 cm^{-1}, the neighboring peaks from the 1370 cm^{-1} becomes less intensive, the 895 cm^{-1} peak becomes more intense, the 1120 cm^{-1} peak becomes a shoulder, the shoulder at 1000 cm^{-1} becomes better resolved and the maximum intensity due to O—H stretching vibration is shifted from 3250 cm^{-1} to 3360 cm^{-1}. These infrared spectral modifications are basically the differences observed between cellulose I and II [9], showing that the cellulose obtained from the cotton residue as well as the Carlo Erba cellulose correspond to cellulose type I. Treating cellulose I with NaOH solution (for α- and β-cellulose determination) results in cellulose II as is well known. A little

TABLE I α- and β-cellulose content of Carlo Erba and cotton residue cellulose

cellulose	*α-cellulose %*	*β-cellulose%*
cotton residue	56	37
Carlo Erba	42	55

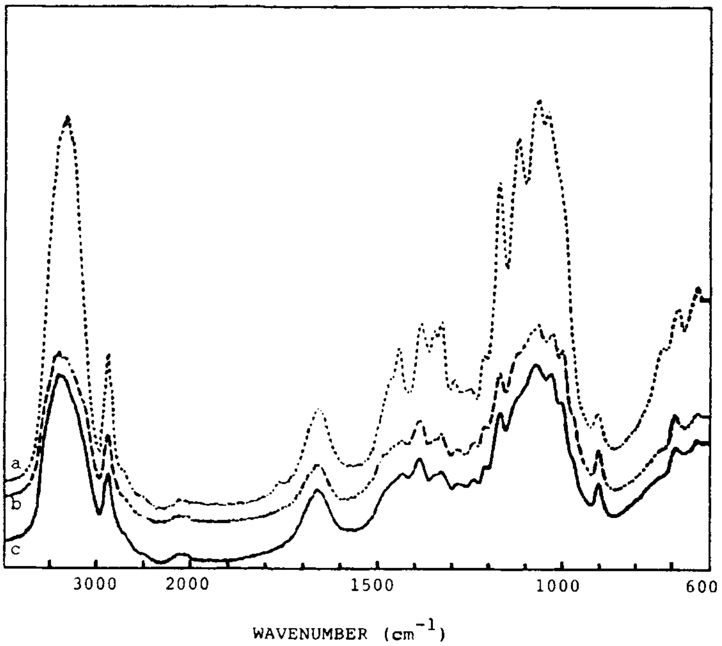

FIGURE 1 Infrared spectra of commercial cellulose (a) and corresponding α-cellulose (b) an β-cellulose (c).

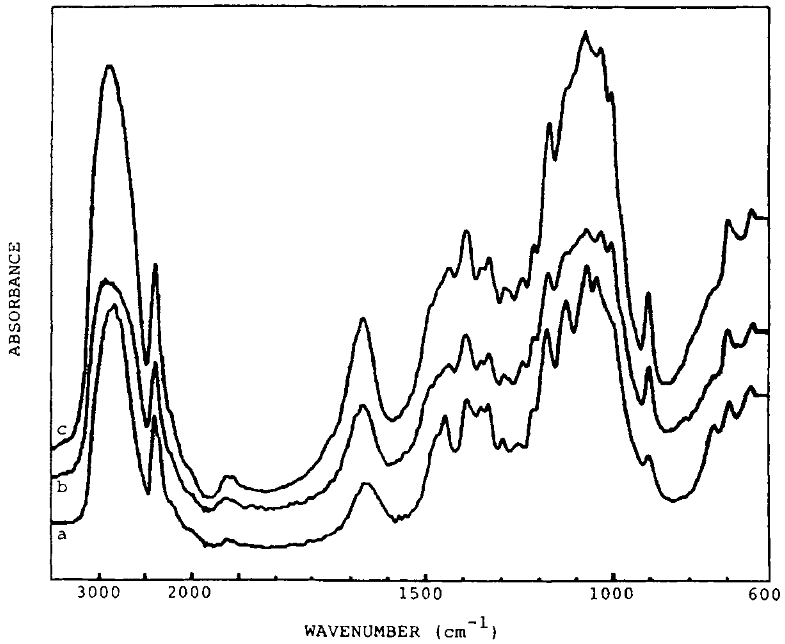

FIGURE 2 Infrared spectra of cotton residue cellulose (a) and corresponding α-cellulose (b) an β-cellulose (c).

difference is also observed between the α- and β-celluloses spectra at the O—H stretching vibration peak at 3360 cm^{-1} that is broader for α-cellulose.

Thermal behavior of these celluloses were analyzed, TGA and DSC curves obtained with the commercial and the cotton residue cellulose are in Figures 3 and 4. Both celluloses show dehydration up to 110 °C with ~ 6% weight loss in the TGA curve and an endothermic peak in the DSC curve. Commercial Carlo Erba cellulose begins to decompose at 275 °C and a second pyrolysis stage initiates at 370 °C. The cotton residue cellulose begins to decompose at 224 °C and at 365 °C initiates a second stage of pyrolysis. For commercial cellulose, an intense endothermic peak was observed in the DSC curve, practically coinciding with the DSC curve from cotton cellulose [10], although the cotton residue cellulose showed not well defined exothermic peaks in the 300–500°C range of temperature. This behavior was assigned to differences in crystallinity and molecular weight, as it is known, they can alter significantly the pyrolysis process [11].

Table II shows the residual weight values at temperatures at which constant weight is attained after complete pyrolysis of the celluloses. Cotton residue celluloses showed higher residual weights than commercial celluloses. There are evidences that the amount of char formed during pyrolysis is directly

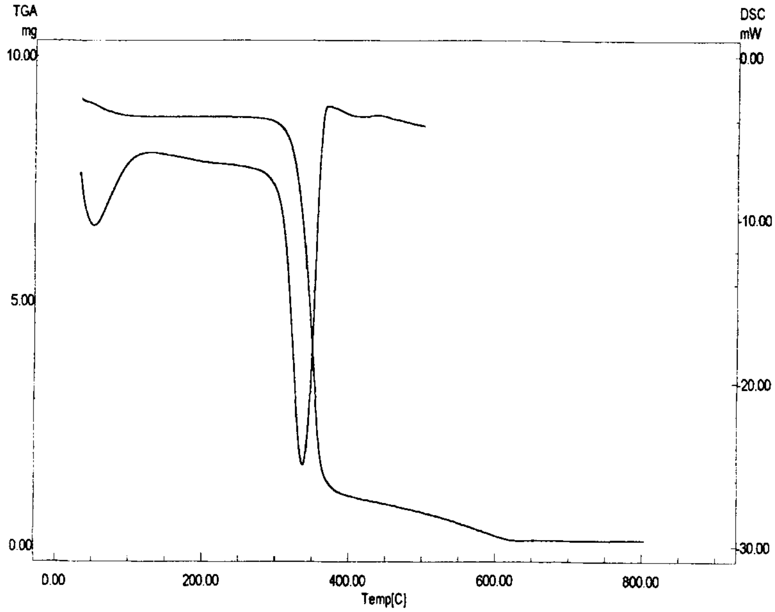

FIGURE 3 TGA and DSC curves of commercial cellulose.

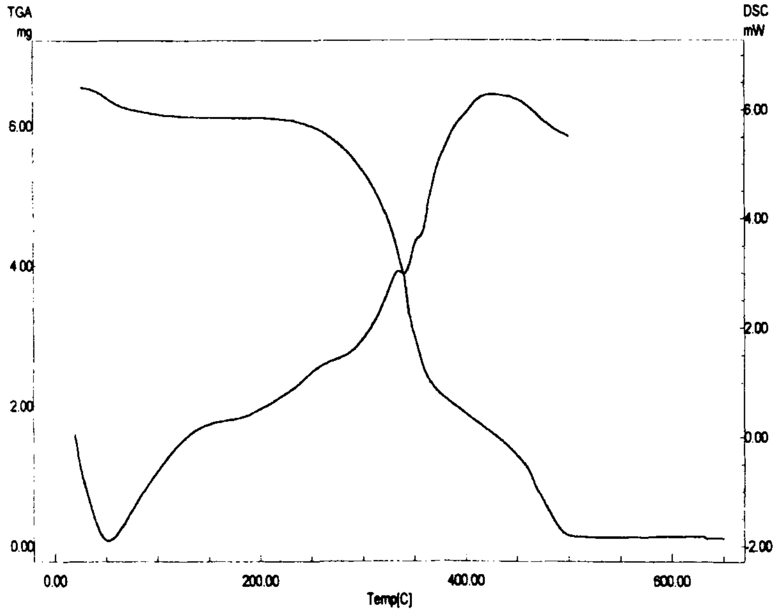

FIGURE 4 TGA and DSC curves of cotton residue cellulose.

proportional to the percentage of less ordered regions in the cellulose sample [10]. Temperatures in Table II and apparent activation energy in Table III indicate a less thermal stability of cotton residue cellulose compared with the commercial cellulose. The same tendency is observed for the corresponding α- and β- celluloses.

The DSC curves (Fig. 5) were similar for the α-celluloses and for the β-celluloses: an exothermic peak for the β-celluloses and an endothermic peak for the α-celluloses in the range of 300–380°C.

TABLE II TGA characteristics of celluloses

Cellulose type	*% Residual weight*	*T_i(°C)*	*T_{max}(°C)*
commercial	1,4	275	348
α-cellulose	1,6	225	353
β-cellulose	2,4	227	344
cotton residue	2,0	224	343
α-cellulose	4,4	212	353
β cellulose	2,7	205	338

T_i: Initial decomposition temperature.
T_{max}: Temperature at which pyrolyisis rate is maximum.

TABLE III Apparent activation energy of the principal pyrolysis reaction of celluloses

Cellulose type	*E_a(kJ/mol)*	*α*	*CC*
Commercial	205.1	0.129-0.835	−0.999
α-cellulose	198.4	0.149-0.758	−0.999
β-cellulose	91.1	0.232-0.535	−0.997
cotton residue	84.9	0.250-40.78	−0.997
α-cellulose	125.6	0.214-0.584	−0.995
β-cellulose	46.9	0.123-0.588	−0.999

α: conversion range considered in each case.
CC: correlation coefficient.

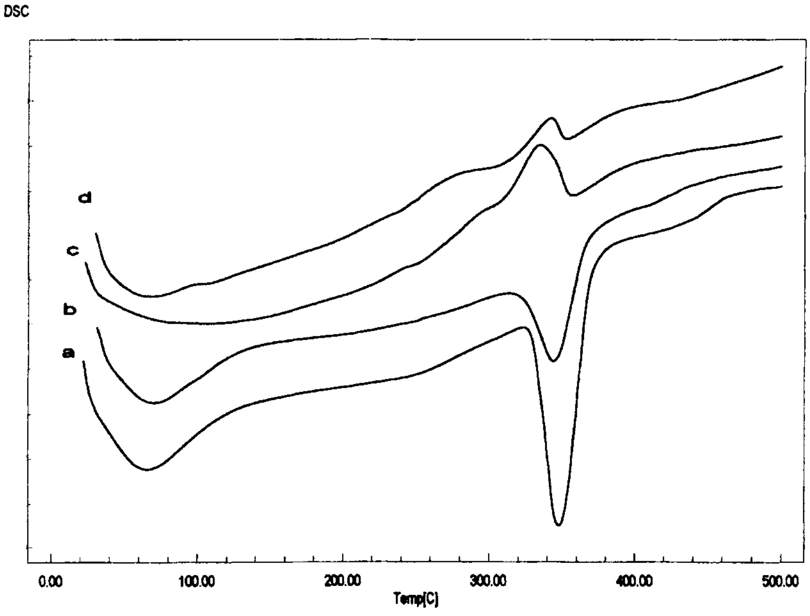

FIGURE 5 DSC curve of α-cellulose (a) and β-cellulose (c) from commercial cellulose; α-cellulose (b) and β-cellulose (d) from cotton residue cellulose.

Benzylcelluloses

Celluloses from Carlo Erba and from cotton residue were benzylated by a Williamson synthesis reaction:

$$\text{Cel-OH} + \text{NaOH} \rightarrow \text{Cel-O}^-\text{Na}^+ + \text{H}_2\text{O}$$

$$\text{Cel-O}^-\text{Na}^+ + \text{ClCH}_2\text{C}_6\text{H}_5 \rightarrow \text{Cel-O-CH}_2\text{C}_6\text{H}_5 + \text{Na}^+\text{Cl}^-$$

Samples were taken from the reaction medium at various reaction times and the substitution degree analyzed by infrared spectroscopy. The substitution of hydroxyl groups by benzyl groups is confirmed in the infrared spectra: O—H vibration absorption at 3420 cm $^{-1}$ diminishes significantly, peaks at 3000–3100 cm $^{-1}$, 1510 cm $^{-1}$, 1450 cm $^{-1}$, 750 cm $^{-1}$ and 710 cm $^{-1}$ appeared due to aromatic groups (Fig. 6).

For relative substitution degree determination the ratio of the absorbances at 750 cm $^{-1}$ and 3420 cm $^{-1}$ were found to be convenient. Results are shown in Figures 7 and 8. Both celluloses attained a maximum benzylation degree at about 10 h of reaction.

TGA curves from benzylcelluloses in Figures 9 and 10 show that pyrolysis occurs in three stages. The temperatures at which the decomposition rates attained maximum values are approx. 350 °C, 505 °C and 610 °C for two benzylcelluloses.

With the objective of verifying how thermal transitions occurs for the different benzylcelluloses synthesized, DSC curves were drawn in the range from 0 to 500 °C (Figs. 11 and 12). An endotherm is observed up to 100 °C for the benzylcelluloses obtained with the lower reaction times, assigned to water evaporation which is also observed in the TGA curves. This endotherm is absent in the benzylcelluloses obtained with higher reaction times because this

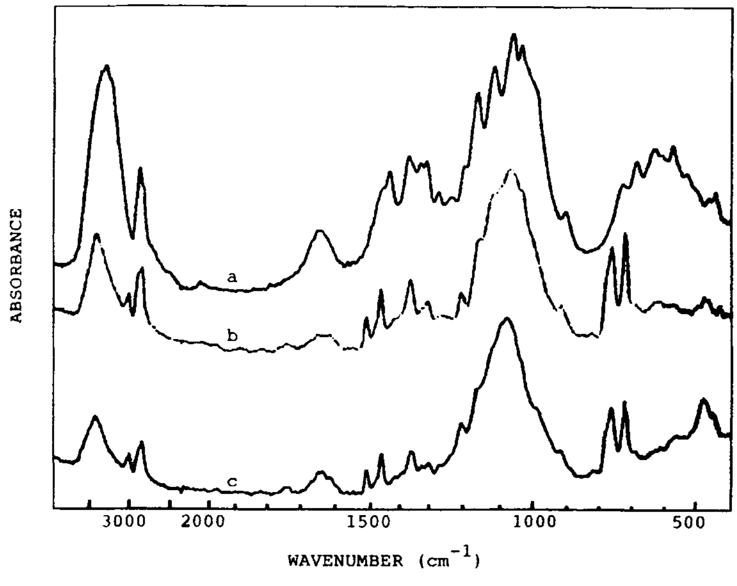

FIGURE 6 Infrared spectra of benzylcellulose obtained with the cotton residue cellulose at (a) 2.5 h, (b) 5 h, and (c) 10 h of reaction times.

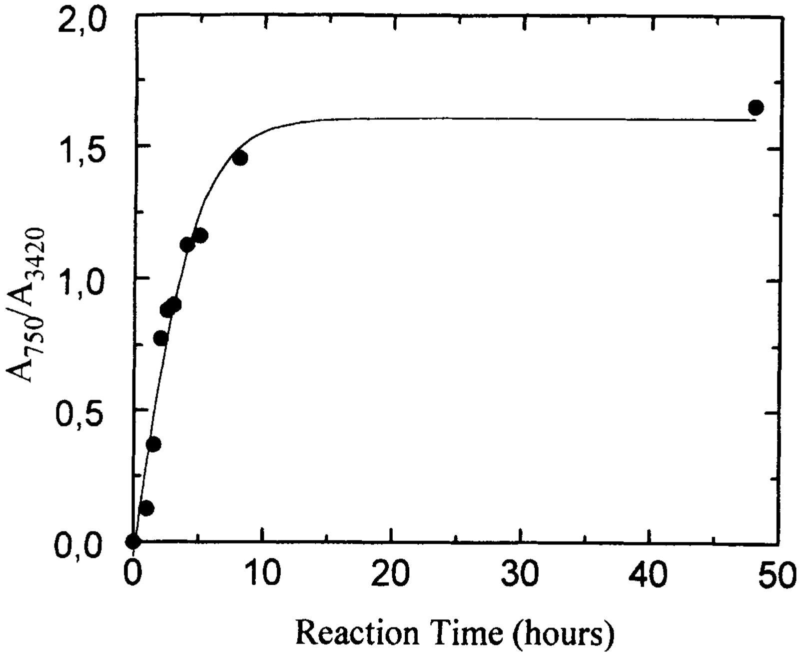

FIGURE 7 Relative benzylation degree (A_{750}/A_{3420}) of benzylcellulose obtained from commercial cellulose.

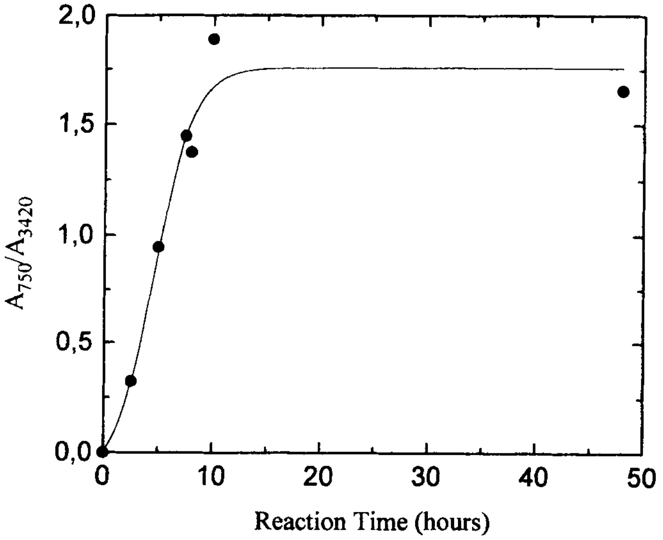

FIGURE 8 Relative benzylation degree (A_{750}/A_{3420}) of benzylcellulose obtained from cotton residue cellulose.

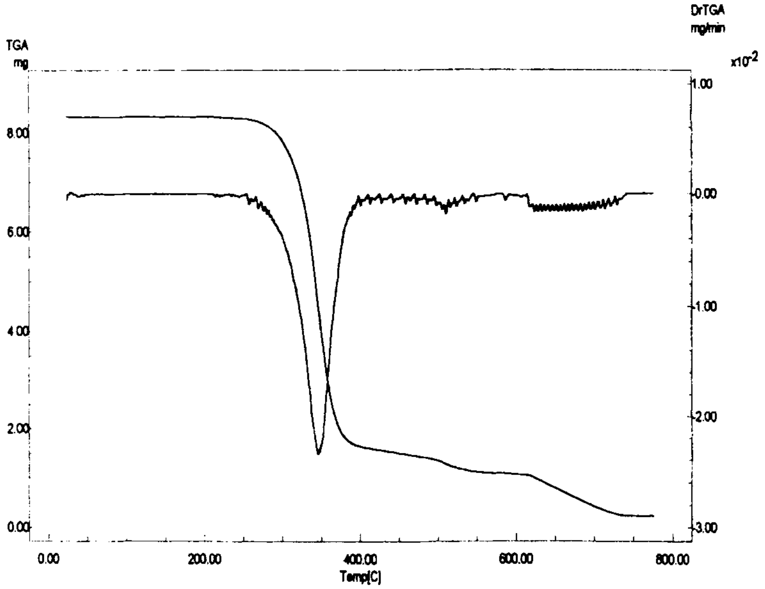

FIGURE 9 TGA and DTGA curves of benzylcellulose from commercial cellulose (8 h of reaction time).

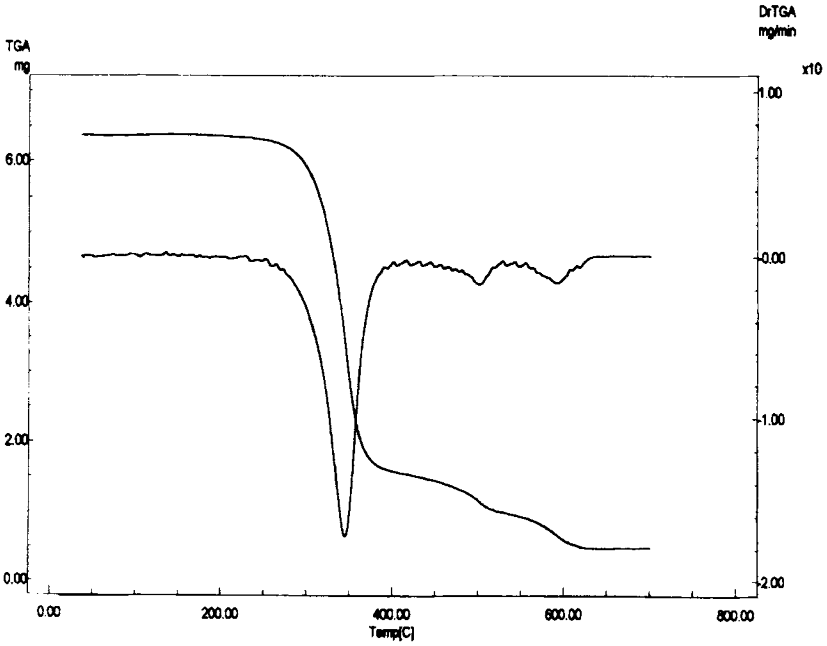

FIGURE 10 TGA and DTGA curves of benzylcellulose from cotton residue cellulose (10 h of reaction time).

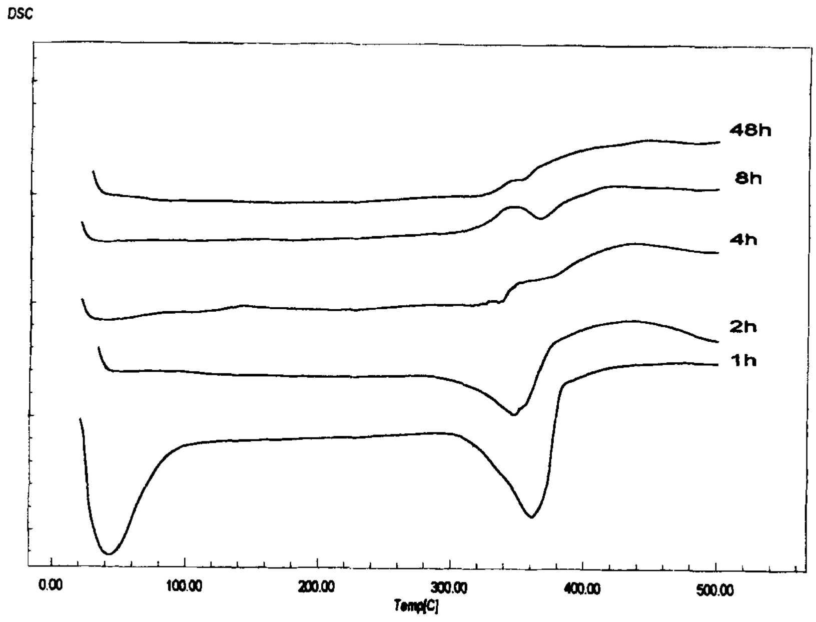

FIGURE 11 DSC curves of benzylcelluloses obtained with different reaction times from commercial cellulose.

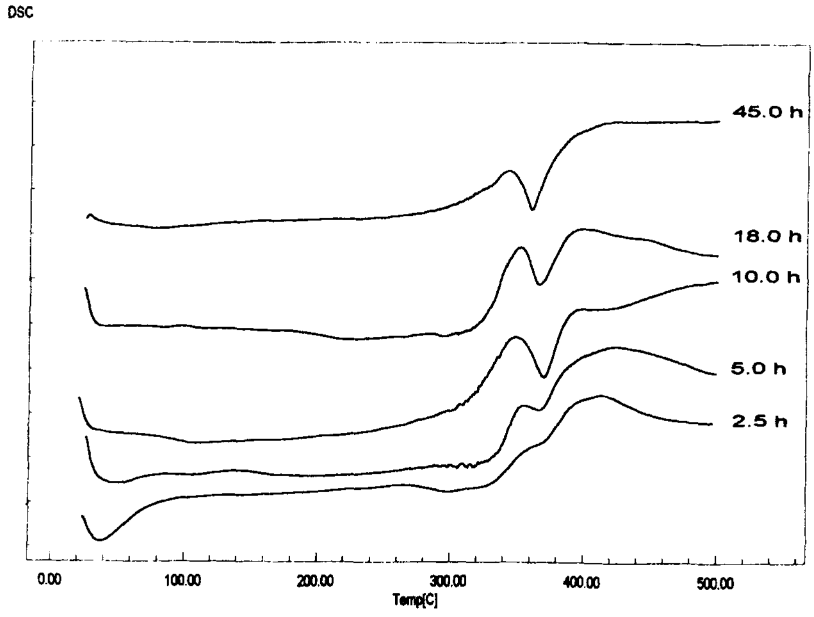

FIGURE 12 DSC curves of benzylcelluloses obtained with different reaction times from cotton residue cellulose.

polymer has an extremely low moisture absorption [5]. In the range from 300 to 400 °C some differences were observed for the various benzycelluloses. For the product obtained from commercial cellulose, the strong endotherm at 350 °C in the original cellulose becomes less intensive and from 4 h of reaction on, two weak endotherms seems to appear. The benzylcelluloses obtained with the cotton residue cellulose show exotherms in the range of 300–450 °C, two exotherms becomes better defined in the curve of the product obtained with 10 h of reaction.

Glass transition was only observed for the benzylcelluloses obtained from 8–10 hours of reaction time on. The glass transition temperatures (Tg) were determined as indicated in Figure 13. T_g data as well as Ti and T_{max} for various benzylcelluloses are in Table IV. They show practically the same tendencies and very similar values comparing benzylcelluloses obtained from cotton residue cellulose and commercial cellulose. Although T_i values of benzylcellulose obtained from commercial cellulose with low reaction times are higher in about 20 °C than the corresponding benzylcelluloses from the cotton residue cellulose.

Apparent activation energies (data in Table V) showed by various benzylcelluloses also indicate a little higher thermal stability for the commercial

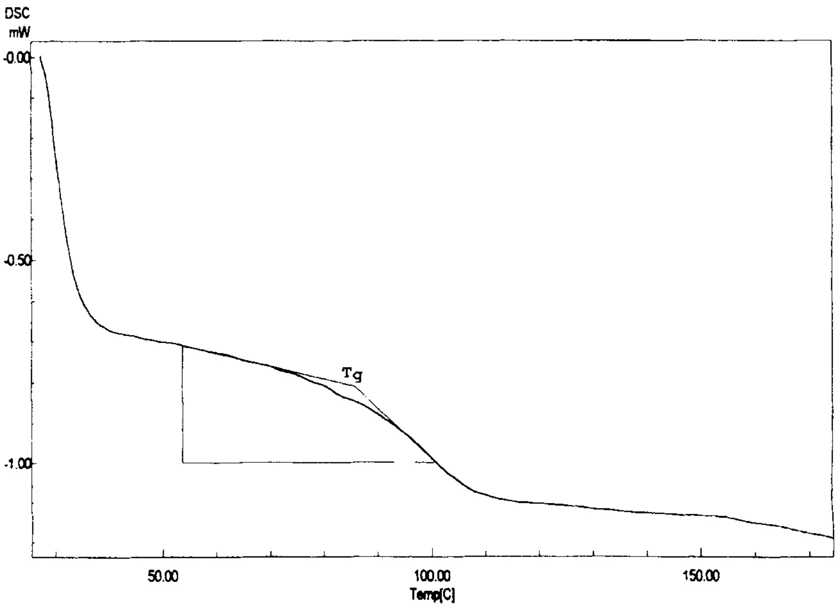

FIGURE 13 DSC curve showing glass transition temperature (T_g) of benzylcellulose from cotton residue cellulose (10 h of reaction time).

TABLE IV Physicochemical parameters obtained from DSC and TGA curves of benzylcelluloses

Benzylcellulose	*Reaction time (h)*	*T_g(°C)*	*T_i(°C)*	*T_{max}(°C)*
from	1.0	–	221	335
Carlo	2.0	–	245	359
Erba	4.0	–	250	342
	8.0	79	218	347
	45.0	69	243	348
from	2.5	–	202	335
cotton	5.0	–	215	358
residue	10.0	85	243	345
	18.0	74	246	344
	45.0	68	225	343

T_g: Glass transition temperature T_i, T_{max}: idem Table II.

TABLE V Apparent activation energy of the principal pyrolysis reaction of benzylcelluloses

Benzylcellulose	*Reaction time (h)*	*E_a (kJ/mol)*	*α*	*CC*
from	1.0	158.0	0.344–0.819	–0.998
Carlo	2.0	152.4	0.292–0.823	–0.998
Erba	4.0	163.5	0.179–0.707	–0.999
	8.0	145.1	0.025–0.692	–0.999
	45.0	138.2	0.117–0.668	–0.999
from	2.5	101.1	0.297–0.734	–0.998
cotton	5.0	210.6	0.146–0.738	–0.998
residue	10.0	143.2	0.073–0.632	–0.999
	18.0	136.7	0.086–0.650	–0.999
	45.0	134.0	0.101–0.742	–0.999

α, CC: idem Table III.

cellulose derivatives obtained with low reaction times. The corresponding benzylcelluloses obtained with the higher reaction times showed very similar thermal stability.

CONCLUSIONS

Cellulose obtained from the cotton residue showed the same infrared spectrum as a commercial cellulose (for chromatography from Carlo Erba), but different thermal behavior most probably due to structural differences, evidenced in the α- and β- cellulose content. Weights of char obtained after complete pyrolysis suggests that the cotton residue cellulose is less crystalline. Apparent activation energies and initial decomposition temperatures also indicate a higher thermal stability for the commercial cellulose.

The cotton residue cellulose obtained was able to be used at the benzylcellulose preparation. Both celluloses, commercial and cotton residue, showed very similar benzylation degree obtained in equal reaction times. Thermal behavior of benzylcelluloses varies significantly for the products with low substitution degree. The products with high substitution degree (obtained with 10 h of reaction or more) show very similar thermal behavior.

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