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# THERMAL CHARACTERIZATION OF BENZYLCELLULOSE DERIVATIVES PREPARED FROM BLEACHED PINUS KRAFT PULP

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## Abstract

The thermal characterization (DSC and TG) of benzylcellulose derivatives prepared from the benzylation of bleached *Pinus Kraft* pulp is described in this paper. The objective of this study was to examine the changes in glass transition temperature ($T_g$) and the thermal stability of the benzylated product as a function of the benzylation extent (degree of substitution). The DSC analysis showed that the benzylcelluloses can display glass transition temperature at two different regions and that thermal stability is slightly higher than that of the parent cellulose.

**Keywords:** benzylcellulose, DSC, glass transition temperature, TG, thermal stability

## Introduction

Development of new polymeric materials from vegetal renewable resources has received great attention in the scientific and technical literature.

Cellulose and cellulosic pulps are the main products of the pulp and paper industry, which employs different wood species as raw material. The utilization of cellulose for the production of thermoplastics materials corresponds to a very small part of the total amount produced by the industry.

Cellulose is a linear high molecular mass polysaccharide composed of anhydro-glucopyranose units linked by β-(1→4) glycosidic linkages. Cellulose chains have a strong tendency to form intermolecular and intramolecular hydrogen bonds [1] due the presence of three hydroxyl groups per each glucopyranose unit. This characteristic inhibits the direct utilization of cellulose as a thermoplastic material [2, 3]. However, the internal plasticization of the cellulosic chains by chemical modification can produce thermoplastic derivates. This chemical modification is normally performed by etherification or esterification reactions. The benzylation reaction was already employed to produce thermoplastic derivatives, which can be ob-

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tained with different degree of substitution by employing different reaction times or particular experimental conditions [4–7].

The thermal degradation of cellulose was dealt with by Carr *et al.* [8]. The properties of the thermoplastics materials obtained by benzylation are the consequence of this particular group and the pattern of the substitution [3].

Hon *et al*. reported the benzylation of wood and found that it was not possible to determine the glass transition temperature by DSC analysis [4]. They attributed this fact to the complex chemical structure of wood. Joaquim studied the thermal behavior of benzylcellulose obtained from the pitch fraction of sugar cane bagasse and determined the glass transition temperatures by DSC experiments. The author reported values in the range of 93 to 105°C [5]. Zemke *et al.* observed glass transition temperatures in the range of 68–85°C for cotton benzylated samples obtained with reaction times varying from 8 to 10 h [6]. Pereira *et al.* reported also the production of benzyl derivatives from sugar cane bagasse, which showed glass transition temperatures in the range of 42 to 75°C for products obtained with up to 6 h of reaction times [7].

The work reported here shows the results obtained in the study of the thermal characterization by DSC and TG analysis of benzylated cellulose derivates prepared from wood pulps and benzyl chloride over various reaction times.

## Materials and methods

### *Benzylation reaction*

2.0 g of dry Pinus ssp. Kraft breached pulp was activated with 35 mL of NaOH 40% solution in a 250 mL flask. This mixture was maintained under mechanical stirring and the temperature gradually increased to 110°C in an oil bath. When the temperature of the mixture reached 110°C, 15 mL of benzyl chloride were added and the reaction was allowed to proceed for various reaction times (30 to 360 min). The reaction products were washed successively with ethanol and water and the excess of benzyl chloride was removed by extraction in a Soxhlet apparatus. The total removal of benzyl chloride was verified by UV/VIS spectroscopy. As final step of the preparation, the samples were dried and pulverized in a laboratory mill.

### *Mass gain determination (Solid-state NMR $^{13}C$ CP/MAS analysis)*

The mass gain of the benzylated samples were determined by Solid-state NMR $^{13}C$ following the procedure described by Opella et al. [8]. The analyses were performed in a VARIAN UNITY 400 spectrometer operating at 100.58 MHz. Spectra were obtained by cross polarization method with magic angle spinning (CP/MAS). The radio frequency strength for cross polarization and decoupling was 50–70 kHz, the contact time was 3 s. The pulse length for the proton was 4 μs, whereas the spectra were obtained with 4096 points. Hexamethylbenzene was taken as secondary reference (aromatic peak at 132.3 ppm from TMS). For each spectrum, 3000–5000 transients were collected. Samples were analyzed in a rotor of zircon of 5 mm diameter and spinning rate about 10 kHz. For the dipolar dephasing measures, repetition time was 3 s, contact time 3 μs and a delay of 3 μs, in decoupling. The degree of substitution (DS) was calculated from the ratio of aromatic to aliphatic carbon atoms (discounting the contribution of the benzylic $CH_2$ group).

### *Thermogravimetric analysis (TG)*

TG measurements were carried out in a Shimadzu TGA-50 instrument from samples of benzylated cellulose derivatives. Approximately 5 mg of sample was weighed and heated from room temperature to 800ºC at 20ºC $\min^{-1}$ under nitrogen flow rate of 20 mL $\min^{-1}$. The data were processed by using the TA50-WS Shimadzu software.

### *Differential scanning calorimetry analysis (DSC) [9]*

The measurements were carried out in a Shimadzu DSC-50 instrument from approximately 5 mg of material (sample on an aluminum pan) under nitrogen flow rate of 20 mL $\min^{-1}$. Each sample was analyzed from three run experiments. The first run was carried out from room temperature to 110°C at 20°C $\min^{-1}$, to remove volatile compounds and to eliminate the thermal history of the samples. The second and third runs were accomplished at 10°C $\min^{-1}$, from –100 to 200°C (to determine the glass transitions temperatures). The experiments were performed in duplicate for each sample.

## Results and discussion

### *Thermogravimetric analysis*

The average degree of substitution (DS) of benzylated cellulose derivatives produced in this work was in the range of 0.26 to 2.72. DS increases with reaction times reaching the higher value for the sample produced with 3 h 30 min to 5 h 00 min reaction time. The sample obtained with six-hour by 6 h 00 min reaction time is less benzylated than the previous ones probably due to the degradation of high benzylated fractions. The mass loss of the benzylated samples shows different patterns according to different reaction times employed in the benzylation reaction (Fig. 1). The low substituted sample (30 min reaction time – DS=0.26) showed a first mass loss step around 100°C, which can be attributed to the elimination of water. At this temperature, breakage of glycosidic linkages can eventually occur, resulting in a decrease in the degree of polymerization (DP) of the cellulose. The second and more pronounced step is due to dehydration reactions with the consequent mass loss due to the evaporation of liberated water and chemical degradation of the glycosidic moieties, producing among other low volatile products, levoglucosan. This low substituted benzylated derivative also shows a third degradation step starting close to 400ºC, with slow mass loss until 800ºC. Above the onset temperature, the pyrolysis of the levoglucosan previously formed and other degradation products occur, producing volatile components that are eliminated [3, 10]. The samples obtained with 3 and 6 h reaction times (degree of substitution of 2.51 and 2.09, respectively) are also shown in Fig. 1 and are

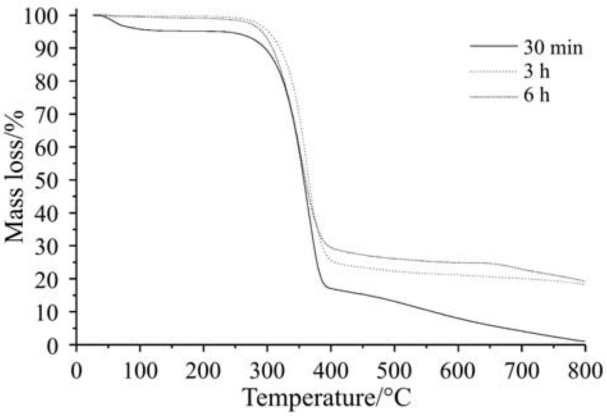

**Fig. 1** TG curves of benzylated samples produced with 30 min, 3 and 6 h reaction time

representative of all samples produced with reaction times higher than 30 min. These samples display a slightly different mass loss pattern. They do not exhibit the initial mass loss due to water evaporation, as they are less hydrophilic materials. On the other hand, the residual mass is higher than that observed for the less benzylated sample. The temperatures at the beginning of the degradation for all samples are in the range of 210–240ºC, which indicates that these materials must be processed at temperatures lower than 200°C. The data of TG measurements are summarized in Table 1.

**Table 1** Results of thermogravimetric analysis of benzylcellulose

| Reaction time | DS (NMR $^{13}$C) | Degradation onset/°C | Degradation endset/°C | Mass loss/% up to 500°C |
|---|---|---|---|---|
| 30 min | 0.26 | 315 | 395 | 86.8 |
| 1 h | 0.65 | 314 | 371 | 90.3 |
| 1 h 30 min | 1.32 | 323 | 377 | 86.7 |
| 2 h | 2.28 | 332 | 388 | 86.8 |
| 2 h 30 min | 2.16 | 328 | 382 | 85.1 |
| 3 h | 2.51 | 315 | 390 | 77.7 |
| 3 h 30 min | 2.72 | 307 | 378 | 71.8 |
| 4 h | 2.64 | 287 | 367 | 72.1 |
| 5 h | 2.60 | 307 | 382 | 60.9 |
| 6 h | 2.09 | 299 | 387 | 73.9 |

The onset temperatures were in the range of 300 to 330ºC being the highest values found for the samples prepared with intermediate benzylation reaction times and the lowest ones registered for the samples with higher reaction times. The endset temperatures were in the range of 370 to 395ºC without any particular correlation with the correspondent benzylation reaction times. The mass loss for the low substituted samples were somewhat higher (85–90%) than that observed for the benzylated samples with higher DS (60–77%). This behavior is the consequence of the different benzylation extent of the samples and could indicate a change in the cell wall structure of the parent cellulosic pulp. That means, lower reaction times leads to benzylation at the surface of cell wall followed by a more deeply modification at higher reaction times disrupting the cell wall structure.

### *Differential scanning calorimetry*

The insertion of benzyl groups on the cellulosic chains promoted by the etherification reaction leads to a decrease in the amount of both intra- and intermolecular hydrogen bonds. The presence of these non-polar groups induces separation of the cellulosic chains and permits less restricted movements of the chains. In this way, typical changes occur in the DSC curves of benzylated derivatives.

Alterations can be seen in the baseline of the curves, but as previously seen before, TG showed no any evidence of decomposition, degradation or other phenomena in the temperature range in which DSC baseline changes occurred. Hence, one can attribute these changes to the occurrence of molecular relaxation movements related to glass transitions.

The glass transition of the parent cellulose is experimentally inaccessible due to thermal degradation that occurs at temperatures higher than 200ºC. Cellulose derivatives containing non-polar substituting groups will show glass transition at lower temperatures. The DSC curves for the benzylated samples produced with reaction times ranging from 30 min to 2 h and 30 min and from 3 to 6 h are shown in Figs 2 and 3, respectively.

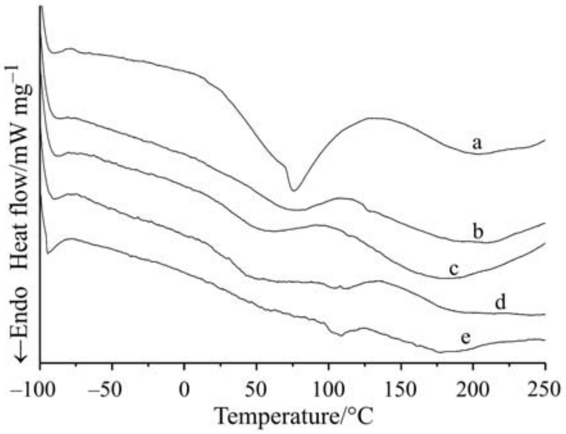

**Fig. 2** DSC curves for benzylcellulose derivatives obtained with different reaction times: a – 30 min, b – 1 h, c – 1 h 30 min, d – 2 h, e – 2 h 30 min

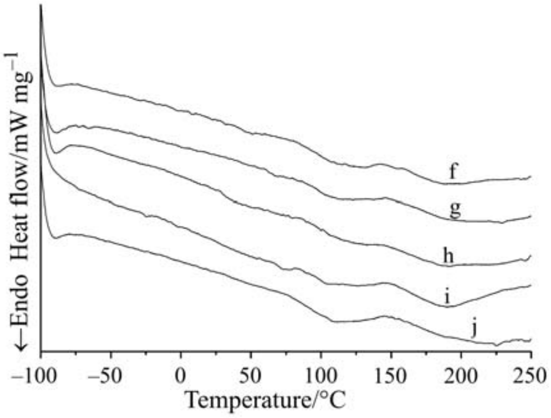

**Fig. 3** DSC curves benzylcellulose derivatives obtained with different reaction times: f – 3 h, g – 3 h 30 min, h – 4 h, i – 5 h, j – 6 h

Glass transition temperatures determined from the changes in the baseline of the curves, as well as their respective values of changes in heat capacity ($\Delta C_p$), are presented in Table 2.

The inspection of the DSC curves revealed the occurrence of glass transitions only in two different temperature intervals (30–40 and 90–100°C). This behavior can be attributed to the different substitution pattern exhibited by the benzylated derivatives once the reactions were performed under heterogeneous conditions and the reaction proceed from the surface to interior of the cellulose fibers.

**Table 2** Glass transition temperatures and $\Delta C_p$ for the cellulose benzylated derivatives

| Reaction time | DS (NMR $^{13}$C) | $T_g$/°C | $\Delta C_p$/J g$^{-1}$ °C$^{-1}$ | $T_g$/°C | $\Delta C_p$/J g$^{-1}$ °C$^{-1}$ |
|---|---|---|---|---|---|
| 30 min | 0.26 | 40 | 0.79 | – | – |
| 1 h | 0.65 | 40 | 0.41 | – | – |
| 1 h 30 min | 1.32 | 36 | 0.28 | – | – |
| 2 h | 2.28 | 36 | 0.43 | – | – |
| 2 h 30 min | 2.16 | 38 | 0.16 | 128 | 0.34 |
| 3 h | 2.51 | 31 | 0.68 | 94 | 0.23 |
| 3 h 30 min | 2.72 | – | – | 100 | 0.09 |
| 4 h | 2.64 | – | – | 98 | 0.21 |
| 5 h | 2.60 | – | – | 102 | 0.09 |
| 6 h | 2.09 | – | – | 88 | 0.20 |

Considering the presence of one or two glass transitions in the different DSC curves and the correspondent temperature intervals where they occurred, it is possible to classify the benzylated samples in three groups:

*1*) One glass transition at 30–40ºC region
*2*) Two glass transitions, at 30–40ºC and 90–130ºC regions
*3*) One glass transition at 90–130ºC region

The benzylated samples that exhibit $T_g$ between 30 and 40°C were produced with lower reaction times (30 min to 2 h). The glass transition observed for these samples can be attributed to the movements of superficial benzylated cellulosic chains with low substitution degrees. The continuation of the benzylation process resulted in an increase of the substitution degree at the surface and starts to promote the benzylation of the chains located inside the cell wall. The glass transition observed at higher temperatures could be attributed to the more benzylated chains, as pointed out by Pereira *et al*. [6]. This behavior was observed for the samples produced with 2 h 30 min and 3 h reaction times. The samples obtained with higher reaction times exhibited only glass transition at 90–130ºC region, which corresponds to the movements of highly benzylated samples.

## Conclusions

The benzylation reaction converted the cellulosic pulp in thermoplastic materials with thermal properties, which can be correlated with the degree of the substitution of the samples. Benzylated derivatives obtained with lower reaction times exhibited glass transition temperature at 30–40ºC while the derivatives obtained with higher reaction times showed glass transition temperatures in the range of 90 to 130ºC. The samples obtained with intermediate reaction times (2 h 30 min and 3 h) showed glass transitions in both temperature ranges. The temperature values of the glass transitions are consequence of the benzylation extent with the higher ones correspondent to higher degree of substitution. The thermal stability of the benzylated samples was somewhat higher than that of the parent cellulosic pulp.

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