J Incl Phenom Macrocycl Chem (2007) 57:75–78
DOI 10.1007/s10847-006-9217-8

ORIGINAL ARTICLE

Grafting of cyclodextrins onto filter paper

Rita C. de Bergamasco · Gisella M. Zanin · Flavio F. de Moraes

Received: 15 May 2006 / Accepted: 20 October 2006 / Published online: 23 January 2007

Abstract Grafting of cyclodextrins and cyclodextrins derivatives on cellulosic surface, such as paper or filter paper, provides hosting cavities that can include a large variety of chemicals for specific cellulose finishing. In this study grafting of monocholorotriazinyl-β-cyclodextrin (MCT-β-CD) and β-cyclodextrin (β-CD) to filter paper has been performed. β-cyclodextrin has been bonded to filter paper using 1,4-butanediol diglycidyl ether as the crosslinking agent. The untreated and treated filter papers were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), demonstrating the covalent binding of cyclodextrins to filter paper. The quantification of β-CD and MCT-β-CD grafted to filter paper was determined by the dye extinction method with the inclusion of phenolphthalein. The final β-CD content amounted to 15.9 μmol per gram of support (1.8% by weight), and 72.8 μmol per gram of support (11.3% by weight) for MCT-β-CD.

Keywords Monocholorotriazinyl-β-cyclodextrin · β-Cyclodextrin · Grafting · Filter paper · DSC · TGA

R. C. de Bergamasco · G. M. Zanin · F. F. de Moraes (✉)
Chemical Engineering Department, State University of Maringa, Av. Colombo 5790, 87020-900 Maringa, PR Brazil
e-mail: flavio@deq.uem.br

Introduction

Cyclodextrins (CDs) are known to form inclusion compounds with a large variety of different molecules. These inclusion compounds are successfully exploited in different fields, such as pharmaceuticals, food manufacturing, and cosmetics [1].

The use of cyclodextrins in the textile applications is a challenge that has been investigated in the last decade. The permanent fixation of cyclodextrins and cyclodextrins derivatives onto cellulosic fibres makes the cavities of the former available and consequently all CD-typical applications are possible [1–3]. A number of approaches in the surface modification by CDs have been reported in the literature [4–8].

This work describes the grafting of monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) and β-cyclodextrin (β-CD) to filter paper. The synthesis products were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Visible absorption spectra were used for determining quantitatively the cyclodextrin content in the samples.

Materials and methods

Materials

MCT-β-CD was a gift from Wacker Chemie GmbH. β-cyclodextrin was supplied by Sigma Chemical Co. The filter paper to be treated with cyclodextrins was 0.205 mm thick and had an areal density of 80 gm^{-2}. All other chemicals were of analytical reagent grade. The water used in the experiments was distilled.

Methods

Chemical bonding of MCT-β-CD to filter paper

Grafting of MCT-β-CD to filter paper was prepared according to a procedure reported by Moldenhauer and Reuscher [6] to treat cotton. Filter paper samples (4 cm × 4 cm) were dipped for 1 min in an aqueous alkaline solution (pH 10) of MCT-β-CD (100 gl^{-1}) and sodium carbonate (10 gl^{-1}) at room temperature, without agitation. The filter papers were dried in an oven at higher temperature, for the fixation of MCT-β-CD. After drying, the paper samples were washed with distilled water, to remove unreacted cyclodextrin, and again dried at 80°C for 1.5 h.

Three main parameters for the fixation of MCT-β-CD to filter paper have been investigated: concentration of the MCT-β-CD solution, temperature and time for fixation of MCT-β-CD to the filter paper.

Chemical bonding of β-CD to filter paper

Filter paper samples (4 cm × 4 cm) were added to 5 ml of a 0.6 M sodium hydroxide solution, containing 10 mg of sodium borohydride, and 5 ml of 1,4-butanediol diglycidyl ether. The reaction was carried out at 25°C for 8 h under magnetic stirring. The samples were washed with distilled water and stabilized with 0.1 M sodium hydroxide solution for 5 min. The treated filter paper was then dried at 80°C for 1.5 h.

The samples treated with 1,4-butanediol diglycidiyl ether were added to 10 ml of 0.1 M sodium hydroxide solution, containing 0.5 g of β-CD. The mixture was stirred at 45°C for 16 h. The samples were then washed with tris–HCl buffer (pH 8, 50 mM) and distilled water. The treated filter paper was dried at 80°C for 1.5 h.

Determination of the MCT-β-CD and β-CD content grafted to the treated filter paper

The concentration of MCT-β-CD and β-CD grafted to the filter paper was determined by the phenolphthalein assay method, in which the color fading of an alkaline phenolphthalein solution is proportional to the quantity of the cyclodextrin derivative present. Samples of the finished filters papers (1 cm × 2 cm) were dipped in a phenolphthalein solution (0.06 mM, pH 10) for 5 min. The color intensity was then measured at 550 nm. With the volume of solution (V) and the mass of treated sample (m), the cyclodextrin concentration was transformed to weight percent by:

$$\%\,\mathrm{CD} = \frac{CVM}{m} \times 100 \quad (1)$$

where C is the cyclodextrin concentration and M is the molar mass of cyclodextrin.

Characterization of the filter paper samples grafted with cyclodextrins

Thermogravimetric analysis (TGA) was performed under airflow (50 $mlmin^{-1}$) using a Shimadzu instrument and the temperature program was set as: 10 °$Cmin^{-1}$ from ambient to 600°C.

Differential scanning calorimetry (DSC) curves were obtained using a Shimadzu instrument. The measurements were performed with an airflow of 50 ml min^{-1} and the temperature program was: 10°C min^{-1} from ambient to 500°C.

Results and discussion

Chemical bonding of MCT-β-CD to filter paper

Experiments with variation in the concentration of the MCT-β-CD solution, temperature and time for fixation of MCT-β-CD to the filter paper were carried out. A MCT-β-CD content of 72.8 μmol per gram of support (11.3 % by weight) in the product was achieved, for the optimal reaction conditions of 5 min at 150°C, and concentration of the MCT-β-CD solution at 100 g l^{-1}. For these reaction conditions, a fixation yield of 17.9% was achieved (Fig. 1).

Better results could be obtained with higher temperatures and times of fixation, but the treated paper became strongly colored because of the yellowing

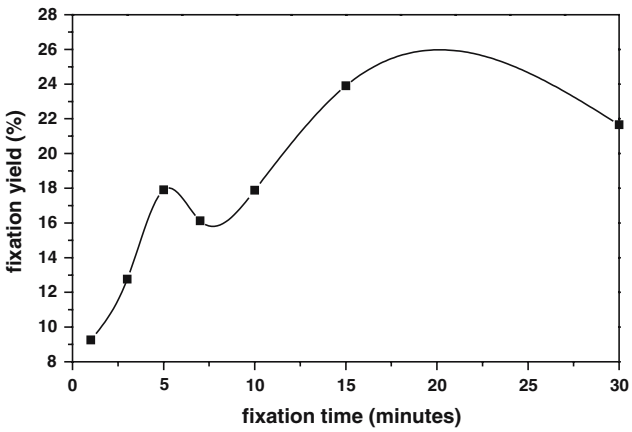

Fig. 1 Fixation yield of MCT-β-CD to filter paper. Reaction conditions: 150°C, 5 min

effect produced by heat. Rehmann et al. [7] studied the covalent bonding of MCT-β-CD to cellulose powder and observed a strong yellowing of cellulose powder when treated with MCT-β-CD at higher temperatures than 140°C, for more than 5 min.

Chemical bonding of β-CD to filter paper

In the process of chemically bonding β-CD to the filter paper using 1,4-butanediol diglycidiyl ether as cross-linking agent, the final β-CD content amounted to 15.9 μmol per gram of support (1.8% by weight).

Characterization of the filter paper samples grafted with cyclodextrins

Differential scanning calorimetry

DSC curves for the untreated and treated filter paper with MCT-β-CD are shown in Fig. 2. The thermogram of the untreated filter paper presents two endothermics peaks: the first at 66.15°C, which corresponds to the dehydration process, and the second at 363°C, corresponding to the decomposition of the cellulose. For MCT-β-CD, there is an endothermic peak at 87.11°C associated with the loss of humidity, and one exothermic peak observed at 256.39°C, that can be attributed to the reaction of the chlorine atom from the triazinyl group with the hydroxyl groups of MCT-β-CD, causing the breaking of the molecule. In addition, at 312°C there is a small endothermic peak that can be associated with the degradation of MCT-β-CD residues.

The DSC curve for the filter paper treated with MCT-β-CD (Fig. 2) show an endothermic peak at 72.33°C due to loss of absorbed water, and a small endothermic peak at 343.68°C that can correspond to the decomposition of the cellulose. The absence of an exothermic peak at 256.39°C, demonstrate the chemical bonding of MCT-β-CD to the filter paper.

Figure 3 shows DSC curves for the filter paper untreated and treated with β-CD. The β-CD thermogram is similar to the filter paper thermogram. The first endothermic peak at 105.65°C, corresponds to the dehydration process, and the second endothermic peak, at 325°C, is associated with the thermal degradation of β-CD.

The thermogram for the filter paper treated with β-CD (Fig. 3) shows an overlap of decomposition peaks of filter paper and β-CD, in the temperature range of 260–400°C, demonstrating the grafting of filter paper with β-CD.

Thermogravimetric analysis

The thermogravimetric curves for the untreated filter paper, MCT-β-CD, β-CD, and filter paper treated with MCT-β-CD and β-CD are shown at Figs. 4 and 5. These curves present three stages of weight loss: the first stage, below 100°C, is associated with dehydration of the samples; the second stage is due the decomposition of samples, and the last stage (above 350°C) is a relatively slow thermal degradation of the sample residues.

As can be observed in Fig. 4 and 5, the samples lose a great amount of weight in the stage of decomposition (245–344°C). The numerical results are presented in Table 1.

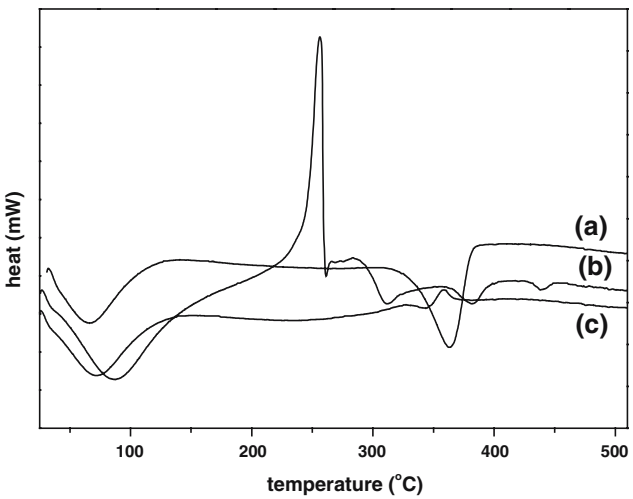

Fig. 2 DSC curves of (**a**) untreated filter paper, (**b**) MCT-β-CD and (**c**) filter paper treated with MCT-β-CD

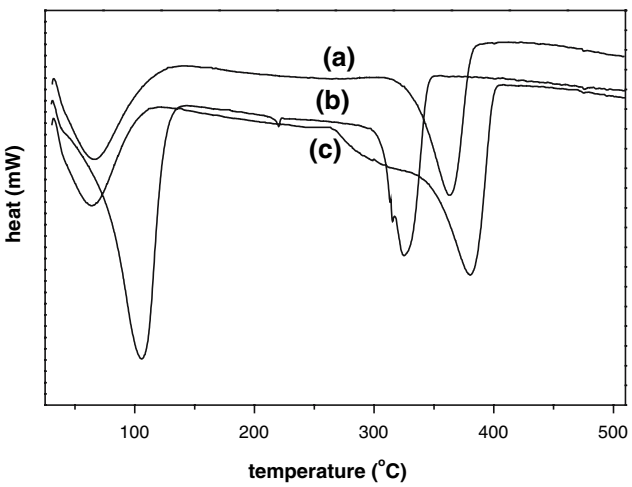

Fig. 3 DSC curves of (**a**) untreated filter paper, (**b**) β-CD and (**c**) filter paper treated with β-CD

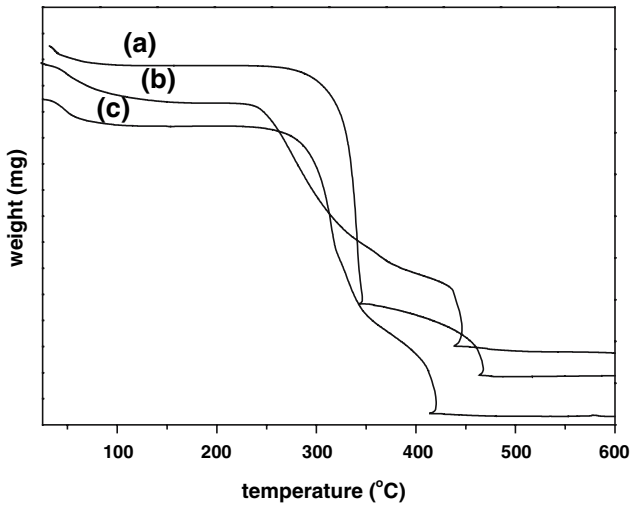

Fig. 4 Thermogravimetric curves of (**a**) untreated filter paper, (**b**) MCT-β-CD and (**c**) filter paper treated with MCT-β-CD

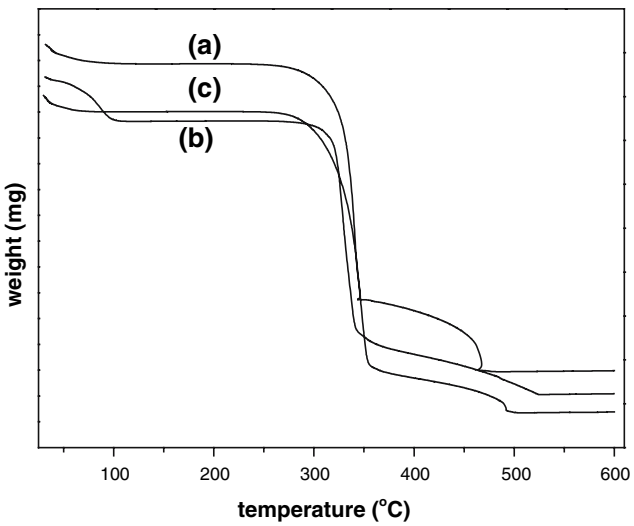

Fig. 5 Thermogravimetric curves of (**a**) untreated filter paper, (**b**) β-CD and (**c**) filter paper treated with β-CD

Table 1 Weight loss of samples in the temperature range 245–344°C

Sample	Weight loss (%)
Untreated filter paper	70.4
MCT-β-CD	38.7
β-CD	65.2
Filter paper treated with MCT-β-CD	54.7
Filter paper treated with β-CD	49.9

The filter paper samples treated with MCT-β-CD and β-CD lose less weight in the temperature range of 245–344°C (Table 1), when compared to the untreated paper, demonstrating the presence of MCT-β-CD and β-CD bonded to the filter paper. This can also be observed in the thermogravimetric curves for the MCT-β-CD and the treated filter paper (Fig. 4) that show a slower mass loss during the decomposition stage, compared to the untreated filter paper curve.

Conclusion

Filter paper was grafted with monochlorotriazinyl-β-cyclodextrin and β-cyclodextrin, in order to include flavors in its future applications. The amount of MCT-β-CD bonded to filter paper was 72.8 μmol per gram of support (11.3% by weight), for a concentration of the MCT-β-CD solution of 100 g l^{-1}, temperature and time of fixation of 150°C and 5 min, respectively. Better results could be obtained at higher temperatures and times of fixation, but a strong yellowing of the filter paper was observed. For β-CD, the amount that was bonded to the filter paper was 15.9 μmol per gram of support (1.8% by weight). DSC and TGA analysis demonstrated the chemical bonding of MCT-β-CD and β-CD to filter paper.

References

1. Lo Nostro, P., Fratoni, L., Baglioni, P.: Modification of a cellulosic fabric with β-cyclodextrin for textile finishing applications. J. Incl. Phenom. **44**, 423–427 (2002)
2. Martel B., Le Thuat P., Crini G., Morcellet M., Naggi A., Maschke U., Bertini S., Vecchi C., Coqueret X., Torri G.: Grafting of cyclodextrins onto polypropylene nonwoven fabrics for the manufacture of reactive filters. II. Characterization. J. Appl. Polym. Sci. **78**, 2166–2173 (2000).
3. Reuscher, H., Hirsenkorn, R., Haas, W.: Patent US 5,728,823. (1998)
4. Garcia, J., Villamarin, S., Tato, J.: Proceedings of the 9th International Cyclodextrins Symposium, Ann Arbor, MI, USA, May 21–24. Publisher Wacker Biochem, Corp. Adrian, MI (2000)
5. Lo Nostro, P., Fratoni, L., Ridi, F., Baglioni, P.: Surface treatments on Tencel fabric: grafting with β-cyclodextrin. J. Appl. Polym. Sci. **88**, 706–715 (2003).
6. Moldenhauer J-P., Reuscher H.: In: Labanderia J., Vila-Jato J (eds.) Proceedings of the 9 th International Cyclodextrins Symposium. pp. 161–165. Santiago de Compostela, Spain (1998) .
7. Rehmann L., Yoshii H., Furuta T.: Characteristics of modified β-cyclodextrin bound to cellulose powder. Starch/Starke **55**, 313–318 (2003).
8. Le Thuatm, P., Martel, B., Crini, G., Maschke, U., Coqueret, X., Morcellet, M.: Grafting of cyclodextrins onto polypropylene nonwoven fabrics for the manufacture of reactive filters. I. Synthesis parameters. J. Appl. Polym. Sci. **77**, 2118–2125 (2000)