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Capture and Controlled Release of Fragrances by CD Finished Textiles

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Abstract

Cotton, wool and polyester fabrics finished with cyclodextrins (by the intermediate of polycarboxylic acids) were impregnated with six different fragrant molecules (β-citronellol, camphor, menthol, *cis*-jasmone, benzyl acetate, geraniol) and citronella oil. The smell intensity of the samples has been investigated during almost one year. In most cases, the odour retention of untreated textiles towards the substrates did not persist over one or two weeks. By contrast, most of the treated samples kept smelling one year after the beginning of the experiment. We observed that the use of polyacrylic acid as crosslinking agent was less effective than citric and butanetetracarboxylic acids. The efficiency of the different CDs varied in the order γ-CD > β-CD > α-CD, and the durability of the fragrant effect was directly dependent on the amount of CD grafted onto the fabrics.

Introduction

Cyclodextrins and their derivatives (CDs) are known to form inclusion complexes with many fragrant molecules [1]. As a matter of fact, *host–guest* type interactions lead to the reduction of the volatility of the substrate whose rate of release is reduced [2]. Thus, one type of application of CDs in the textile domain can consist either to capture the unpleasant smells like those induced by perspiration, or to promote the controlled release of a perfume [3]. The incorporation of CDs onto textile supports can be carried out by impregnation or spraying the fabric with a CD solution, or by permanent fixation onto the fibers by using physicals or chemicals means. The later solution has the advantage that CD can resist to handling and washing cycles, so that complexing properties become intrinsic to the fabric itself. The advantage of this approach is that the support can undergo a certain number of cycles of use without loosing its specific properties. The aim of the present study was to demonstrate that fabrics finished with cyclodextrins, according to the polycarboxylic acid (PCA) method [4–6] are applicable in the odour retention application. Three different types of textile fibers have been grafted with the three current native CDs, by using three different PCA. We also determined the influence of the grafting rate of the fabrics that were finished with variable amounts of CDs.

Experimental

Polyester (PET), wool and cotton woven fabrics have been finished with CDs according to a method previously described [4]. PCA such as citric (CTR), butanetetracarboxylic (BTCA) and polyacrylic (PAA) acids (Aldrich, Milwaukee) were used as grafting agents. Supports underwent 3 degrees of grafting (low, medium, high) by α, β or γ-CD (CDs), a gift from Wacker Chemie GmbH (Burghausen) as reported in Table 1. The grafting rate of the samples is expressed as the weight gain (%-wt) upon the grafting reaction with PCA and CDs. Series of different modified and unmodified fabric samples were impregnated with β-citronellol, camphor, menthol, cis-jasmone, benzyl acetate, geraniol (Aldrich, Milwaukee) and a commercial citronella oil. Fabrics were impregnated in water-alcohol solutions of these perfumes and then roll-squeezed with a padder. The smell intensity of the samples was then evaluated (blind method) by a panel of experimenters at regular intervals during almost one year. A value of the smell intensity was then attributed to each sample according to a scale from 4 (very strong smell) to 0 (no smell).

Alternatively, we also exposed polyester made fabrics to an atmosphere saturated with citronella in a closed desiccator kept at 50 °C during 24 h. The thus perfumed fabrics were then dipped into warm water at 30 °C while stirring during 1 min and dried. Their smell was then evaluated. This procedure was repeated in order to investigate the resistance of the odour against the successive washings.

Result and discussion

It is observed in Figures and 2 that the odours of citronella and camphor were no more detected after 31 and 7 days respectively for the non modified supports, while a rather high level of scent was still measured after almost one year for

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Table 1. Description of the fabric samples, and their grafting rate expressed in %-wt

Support	Fiber	Crosslinking PCA	Type of CD	Graft %-wt
WCG1				4
WCG2	Wool	CTR	γ	8
WCG3				12
PCG1				6
PCG2			γ	10.5
PCG3	PET	CTR		13.5
PCA3			α	8
PCB3			β	12
CCG1				8
CCG2			γ	11.5
CCG3				13.5
CCA3	Cotton	CTR	α	12.5
CCB3			β	12.5
CPG3		PAA		11
CBG3		BTCA	γ	18

Nomenclature of the samples: first letter = type of fibre (W = wool, P = PET, C = cotton); second letter = type of crosslinking agent (C = CTR, B = BTCA, P = PAA); third letter = type of grafted CD (A = β-CD, B = β-CD, G = β-CD); ending number = degree of grafting (1 = low, 2 = medium, 3 = high).

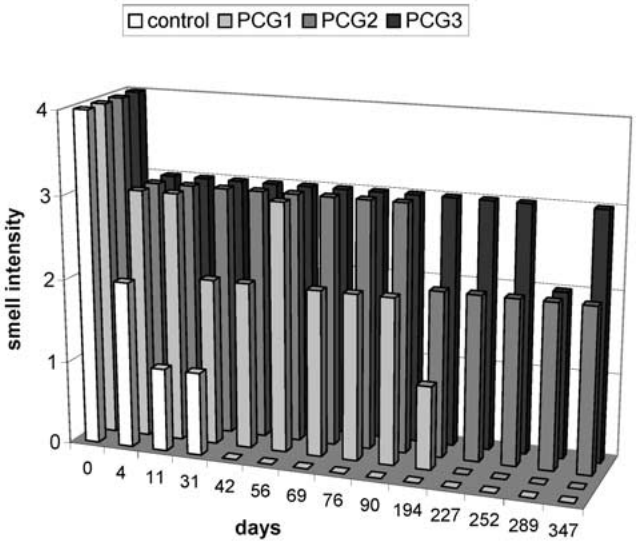

Figure 1. Odour intensity values for PET supports grafted with no, low, medium and high amounts of γ-CD and CTR and impregnated with citronella oil.

some of the CD finished samples. For example, the odour of PET fabrics functionalised with γ-CD and perfumed with citronella oil and camphor remained unchanged after 347 and 308 days, respectively.

Besides, cotton fabrics finished with CDs also presented an improvement of their odour retention capacity, especially towards menthol (Figure 3). Nevertheless it was observed that the effect of the CDs finishing of cotton was not so spectacular than that observed with PET, as illustrated in Figure 4 (geraniol) and Figure 5 (benzyl acetate). Though, rather positive results have been experimentally observed for the other substances (not shown).

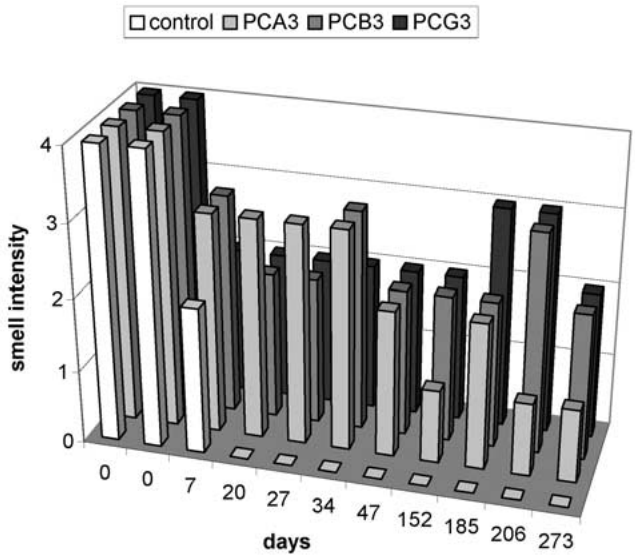

Figure 2. Odour intensity values for PET supports grafted with high amounts of α, β and γ-CD and CTR impregnated with camphor.

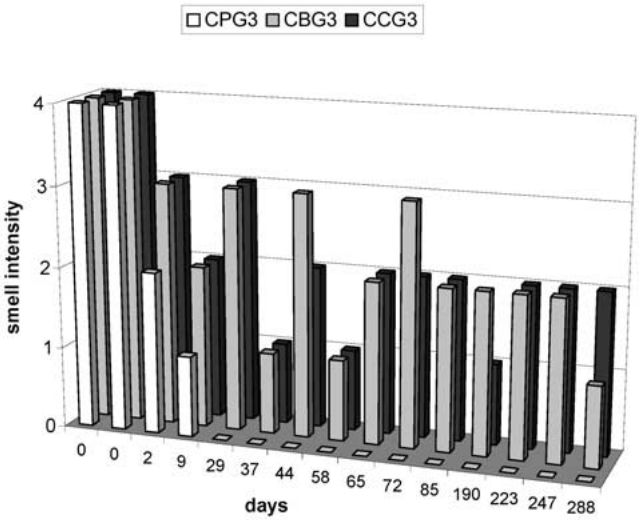

Figure 3. Odour intensity values for cotton supports grafted with a high amount of γ-CD by the intermediate of PAA, BTCA and CTR impregnated with menthol.

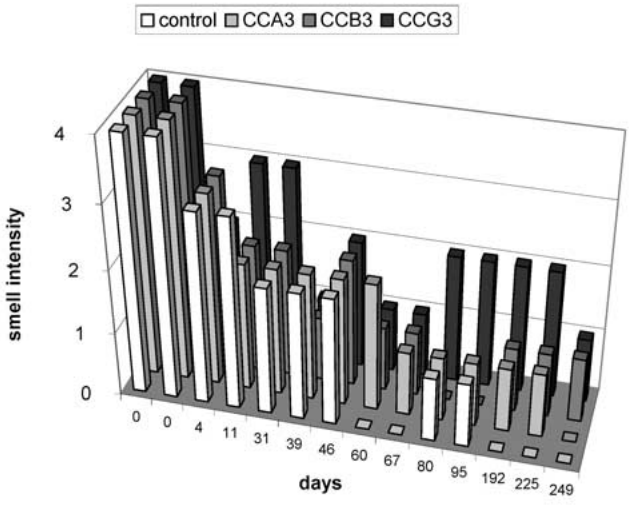

Figure 4. Odour intensity values for cotton supports grafted with high amounts of α, β and γ-CD and CTR impregnated with geraniol.

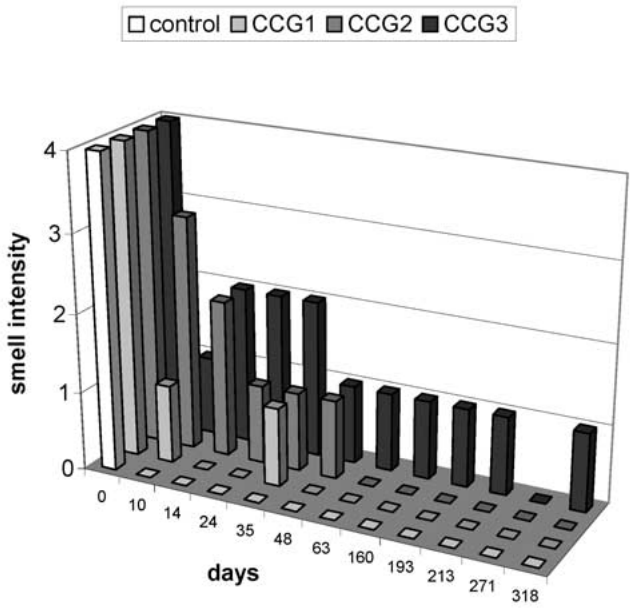

Figure 5. Odour intensity values for cotton supports grafted with no, low, medium and high amounts of γ-CD and CTR impregnated with benzyl acetate.

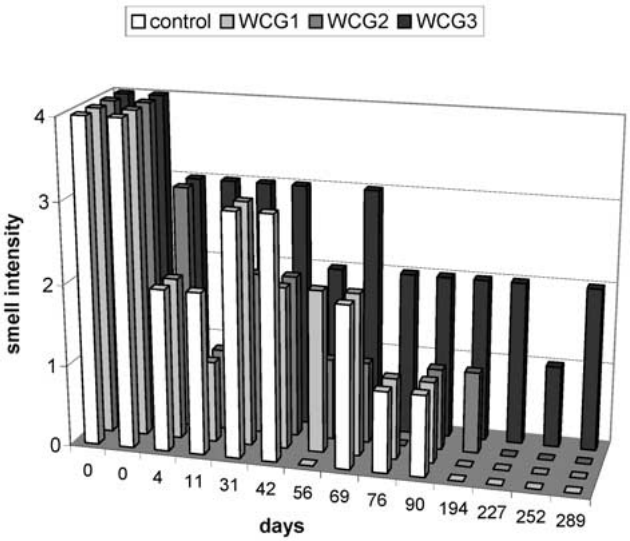

Figure 6. Odour intensity values for wool supports grafted with no, low, medium and high amounts of γ-CD and CTR impregnated with citronella oil.

At last, the difference of odour retention between treated and untreated wool samples was more difficult to observe in the overall experiment, excepted in the case of citronella oil (see Figure 6).

As a matter of fact, one can summary from the above mentioned results that the perfume retention for raw fabrics followed the order cotton $>$ wool $\gg$ PET. Moreover, the CDs finishing of the fabrics enhanced and deeply modified their initial properties so that the above mentioned classification was modified as following : PET $\gg$ cotton $>$ wool.

As represented in Figure 3, the use of PAA as crosslinking agent offered the worse results, compared to CTR and BTCA. In addition, the treatment of cotton by PAA and CDs could even lower the retention properties to a level inferior to that of the control fabric. Generally, we observed that whatever the support and the nature of the fragrance, PAA was the less favourable reagent. On the contrary, the use of CTR and BTCA always resulted in positive and comparable results.

Table 2. Comparison of the relative performances of textiles functionalised with α, β or γ-CDs

Fiber	Cotton			Pet		
cyclodextrin	α	β	γ	α	β	γ
menthol	+	++	++	+++	++	++
camphor	+	++	++	++	+++	+++
citronella	+	+	++	+++	+++	+++
cis jasmone	++	++	++	++	++	+++
b-citronellol	+	++	++	+++	+++	+++
benzyle acetate	+	++	++	+	++	++
geraniol	0	0	+	++	++	+++

+, ++, +++ : respectively no, weak, strong and excellent improvement of the retention capacity.

As observed in Figures 1, 5 and 6 (and confirmed with all five other perfumes of this study), the most persistently perfumed fabrics are those that contain the maximum of grafted CD. So, there is a direct relation between the amount of fixed CDs and the durability of the effect. It is to be mentioned that wool and cotton fabrics grafted with PCA (and no CDs) always gave results close to those of the controls.

The relative performances of PET and cotton supports functionalised by the three different CDs have been evaluated and are reported in Table 2. The general order of the performances is β-CD = γ-CD $>$ α-CD on cotton and γ-CD $>$ α-CD = β-CD on PET. Therefore, γ-CD seems to be the most versatile cyclodextrin with regard to the panel of substrate molecules tested in this study. It is supposed that γ-CD, which presents the most opened cavity, remains more accessible to the substrates despite the crosslinking reaction that occurs upon grafting. In this connection, it is evident that the grafting reaction of CDs onto the fibrous matter implies a certain modification of the accessibility of their cavities. So, the formation constant of the inclusion complexes is probably very different when measured in solution with native CDs, and with CDs immobilised onto a solid matter. As the consequence, it is impossible to establish and to foresee if a given fragrance will be effectively adsorbed and released by the support. The results obtained in the present study show that the odour retention capacity of the CDs finished textiles do not only depend on the CDs-substrates specific interactions, but also depend on non specific interactions between the fiber and the same substrates.

In Figure 7, a smell intensity of 3 units on the fabrics immediately after their exposition to an atmosphere saturated with citronella oil shows that CDs finished fabrics had an improved capacity to capture a perfume under its volatilised form. Furthermore, we report in Figure 7 that such supports also present an improved resistance of their smell to dipping cycles in warm water. One can observe that the odour of

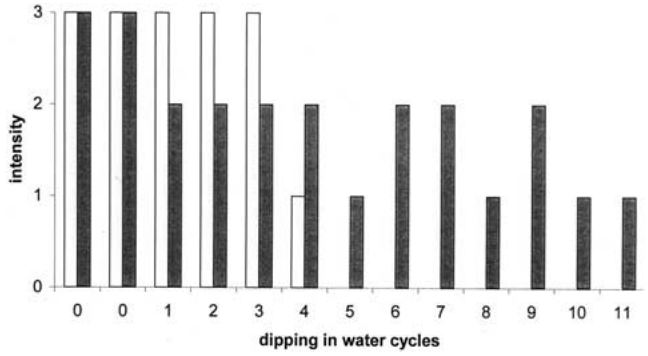

Figure 7. Resistance of citronella smell on control fabric (empty bars) and γ-CD grafted PET fabric (full bars) to successive batches of 1 min at 30 °C.

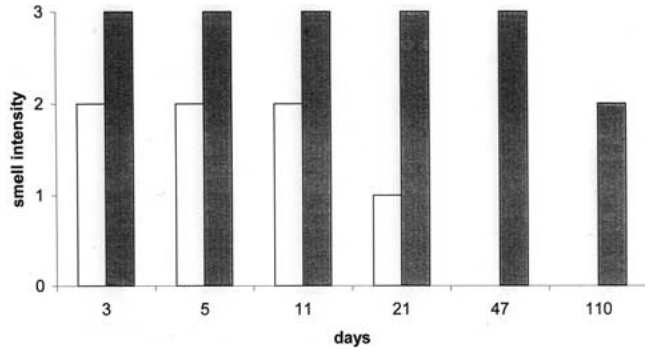

Figure 8. Odour intensity values against time for PET supports. Control sample (empty bars) and sample grafted with β-CD and CTR (full bars) perfumed by volatilisation of citronella oil.

the control sample remained stronger than the CDs finished ones within the 3 first batches, but rapidly disappeared after the fourth one. On the other hand, the citronella smell remained resistant to 12 batches. In consequence, these results show that textile finishing with CDs can also improve the durability of the fragrances against washings.

Finally, we also evaluated the time durability of the smell of the samples perfumed by volatilisation of citronella oil. Figure 8 represents the odour intensity values within a period of 110 days after the samples were put in presence of the fragrance. One can observe that the modified PET fabric remained intensively present within this period, while the odour of the control definitely disappeared between day 21 and day 47. So, it is clear that CDs finished fabrics present a good capacity to trap volatile molecules present in the atmosphere and furthermore, that they are capable to slowly release the entrapped substrates.

Conclusion

It was observed that textile finishing with CDs sharply increased the period of release of perfumes, especially from polyester made fabrics. γ-CD is the most versatile of the three native CDs tested while CTR and BTCA crosslinking reagents present the same qualities. Fabrics can be charged in fragrances by immersion in their water-alcohol solution and can also efficiently capture the volatilised compounds in the atmosphere. It was also observed that the textile finishing with CDs could improve the resistance of the odour to washings with water. So, this work confirmed that the CDs grafted by the intermediate of PCA keep most of their original complex forming properties. However, we have observed that the fragrance retention phenomenon was not only due to *host–guest* complexation, but was also dependant from non specific interactions of the substrates with the surface modified fibers. The term of controlled release is justified by the fact that it will be possible to tailor the desired effect by choosing the most appropriated CD, and by adjusting the amount of CD to graft onto the fabrics dependently from the substrate to capture or to release.

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