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Finishing of Polyester Fabrics with Cyclodextrins and Polycarboxylic Acids as Crosslinking Agents

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Abstract

CDs were grafted onto PET fibers by the intermediate of polycarboxylic acids that played the role of crosslinking agents. We evidenced that grafting occurred despite that no reaction could happen between the polycarboxylic acids and PET. It was concluded that the mode of grafting occurred through the formation of a crosslinked copolymer between PCA and CDs. This copolymer was not covalently fixed to the fibers, but physically adhered or was entangled into the fibrous network so that grafting was resistant to washings and was permanent. We report that the grafting rate depended on (i) temperature of curing; (ii) time of curing; (iii) the ratio PCA/CD. In the most drastic conditions, the weight increase of the fabrics due to the graft reaction could reach 25–30%-wt. α, β, γ-CDs and HP-β-CD successfully reacted but not RAMEB because of its reduced number of free hydroxyl groups available for the esterification reaction.

Introduction

The use of cyclodextrins and their derivatives (CDs) in the textile domain is a challenge that raised in the early 80's [1]. The complex forming properties of CDs towards a multitude of organic substances, such as fragrances, drugs, biocides etc. represent new functionalities for the textile supports, new possibilities of applications and new markets to explore. The permanent binding of CDs onto textile fibers present the advantage that the above mentioned properties of CDs become intrinsic to the modified fiber. Firstly, Szejtli *et al.* reported the grafting of CDs onto cellulose fibers by using epichlorohydrin as crosslinking agent [1]. Buschmann *et al.* claimed the incorporation of CDs into natural or synthetic matters by a physical mean or by chemical paths involving CDs derivatives carrying aliphatic and aromatic groups, chloro carboxylic acids, chloro amino and dimethylol bifunctional compounds as linking agents [2]. Besides, Denter *et al.* [3] and Reuscher *et al.* [4, 5] fixed a monochlorotriazinyl β-CD derivative onto different polymer materials including cotton fibers. At last, we recently proposed a method for the grafting of CDs onto polypropylene nonwoven fabrics by using the electron beam technology [6–8]. Furthermore, in another recent study, we have proposed the possibility to fix CDs permanently to cotton and wool fibers by using polycarboxylic acids (PCA) as binding and crosslinking agents [9, 10]. This method was inspired from the works of Welsh *et al.* who used this family of compounds in the crosslinking reaction of cotton applied to the durable press finishing processing [11]. We observed that CDs were covalently linked to the fabrics by the intermediate of the PCA that esterified (or amidified) at the same time with the OH (or NH_2) groups of fibers and those of CDs. This reaction occurred in the dry state, during a thermofixation step that was carried out above 140 °C.

The present paper consists to report the results obtained in a study that aimed to apply the above mentioned chemical path onto polyester made fabrics. We describe the study of the parameters involved in this particular textile processing. These parameters include the curing conditions (temperature, time) and also the nature of the reactants. The latter consist of three PCA: 1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid (CTR) and polyacrylic acid (PAA) used as crosslinking agents; sodium dihydrogen hypophosphite (NaH_2PO_2) was used as catalyst; α, β and γ-CD and the hydroxypropylated and methylated β-CD derivatives have been tested.

Materials and methods

Polyester (poly(ethyleneterephtalate), PET) woven fabric (surface weight = 110 g/m^2, wet pick up = 180%-wt) has been supplied by Chomarat Frères (Le Cheylard, France). α, β, γ-CDs and the methylated derivative of β-CD in positions 2 and 6 (RAMEB, average DS = 0.62) were gifts from Wacker Chemie GmbH (Burhausen, Germany). Hydroxypropylated β-CD (HP-β-CD, DS = 0.5) was a gift from Roquette (Lestrem, France). PCA such as citric, butanetetracarboxylic, polyacrylic (M_w = 2000 g/mol) and sodium dihydrogen hypophosphite were Aldrich chemicals (Milwaukee, WI, USA). The textile finishing equipment

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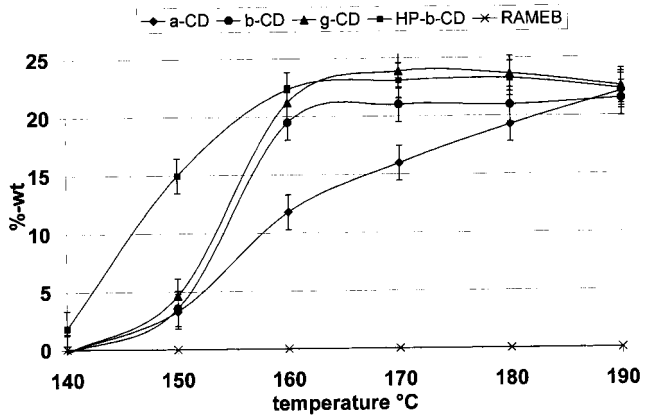


Figure 1. Study of the influence of the curing temperature. CTR as crosslinking agent and the different CDs; [CTR] =100g/L; [NaH_2PO_2] = 10 g/L; [CDs] = 100 g/L.

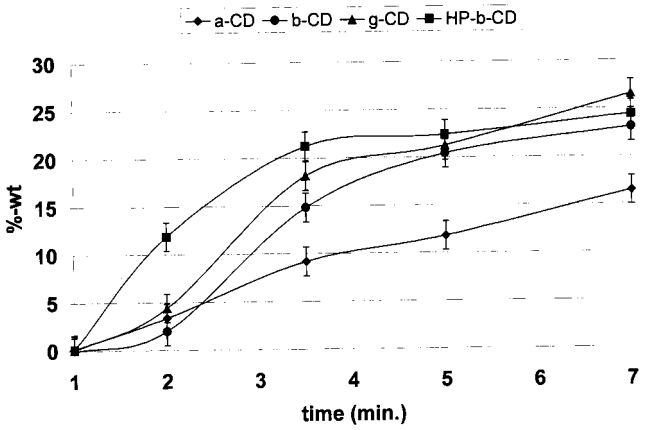


Figure 2. Kinetic study of the grafting with CTR as crosslinking agent and the different CDs. Curing at 160 °C; [CTR] = 100 g/L; [NaH_2PO_2] = 10 g/L; [CDs] = 100 g/L.

consisted of a padder and a thermofixation oven (Roaches, Leek, UK). Fabrics were impregnated by the aqueous solution that contained the reactants, roll-squeezed, dried and thermofixed (at variable temperature and time) and finally washed several times with warm water, until water was clear. Raw and treated samples were dried 30 min at 104 °C before being weighted. The grafting rate was calculated by the following equation: %-wt = $(m_f - m_i)/m_i \times 100$. The precision on the weight gain measurements was ± 1.5 %-wt.

Results and discussion

A preliminary experiment consisted to carry out the finishing of polyester fabrics by the PCA. The result was that we could not observe any reaction, as it could be expected. This can be explained by the fact that PCA cannot intrinsically react with PET that does not carry any free reactive groups. This result was in opposition with what we had previously observed on cotton and wool that readily reacted with PCA [10].

Besides, PET fabrics treated by a mixture of PCA and CDs resulted in a weight increase of the samples. We could confirm that a permanent grafting occurred as this value did not vary upon the successive washings. For example, solutions containing the native CDs and the β-CD derivatives mixed with CTR have been prepared in order to carry out the finishing of fabric samples at different thermofixation temperatures. As reported in Figure 1, results were successful, excepted in the case of RAMEB. As direct linking of CDs onto the fibers has been proved to be impossible in the aforementioned experiment, we deduced that the reaction occurred through the polyesterification between CTR and CDs. It is supposed that the formed copolymer physically adhered or was even entangled into the fibrous network so that grafting was resistant to washings and was thus permanent. Such a type of copolymer, whose mechanism of synthesis is described in Scheme 1, has already been selectively prepared and characterised in a parallel work [12, 13].

In addition, Figure 1 also displays that the reaction occurs in the range 140 °C to 160 °C, excepted for α-CD for which T° has to be increased until 190 °C to attain the maximum grafting rate.

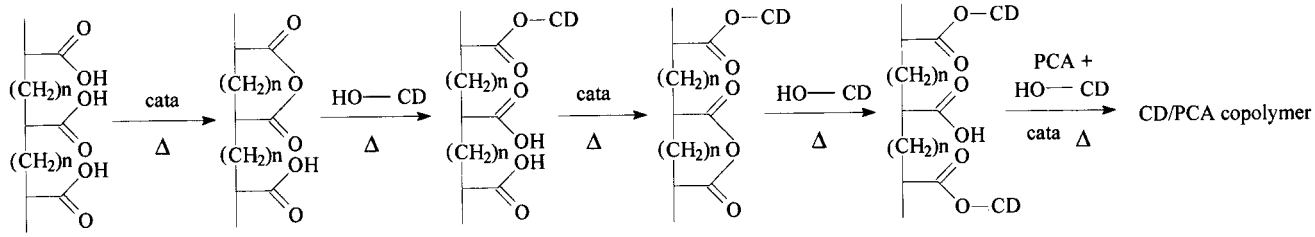
On the other hand, as displayed in Figure 1, RAMEB is not compatible with the present processing method. As previously reported [10], this phenomenon is due to the reduced free esterificable OH groups of this β-CD derivative. For that reason, RAMEB has been discarded from the following experiments.

The kinetic of the reaction has been measured at 160 °C and the related curves are presented in Figure 2. One can observe that the weight gain varies in the order HP-β-CD > γ-CD > β-CD > α-CD, especially in the increasing portion of the curves. This can be explained by the differences of molecular weights of the different CDs that vary in the same order. On the other hand, at higher temperature, the curves (excepted that of α-CD) tend to reach the same plateau value that corresponds to the maximal conversion of the reactants preliminarily impregnated onto the fabric. As a matter of fact, the maximal reaction rate is dependant from the uptake of the textile support in reactants that is imposed by the concentration of the solution and also by the value of the wet pick up.

Besides, it is also observed that HP-β-CD necessitates the lowest reaction time for attaining a definite grafting rate. This is to be attributed to the presence of some hydroxyl groups on the hydroxypropyl substituents that play the role of spacers that facilitate the esterification reaction. On the contrary, it is hardly explainable why α-CD presents a lower reactivity than β and γ-CD.

Lastly, the combination of the results of Figures 1 and 2 allowed us to establish a direct correspondence between temperature and the time of the thermofixation for 140 < T° < 170 °C and for $1 < t < 7$ min. Such data are useful and convenient in order to determine the experimental conditions for the obtaining of a chosen functionalisation rate of the fabrics by fixing either the temperature or the duration of the thermofixation step.

We varied the concentration in CTR in the impregnating bath (0 < [CTR] < 100 g/L) and kept the CDs concentration constant (100 g/L). The weight gain of the fabrics was plotted against the molar ratios in Figure 3. It is ob-



Scheme 1. Copolymerisation reaction between PCA and CDs.

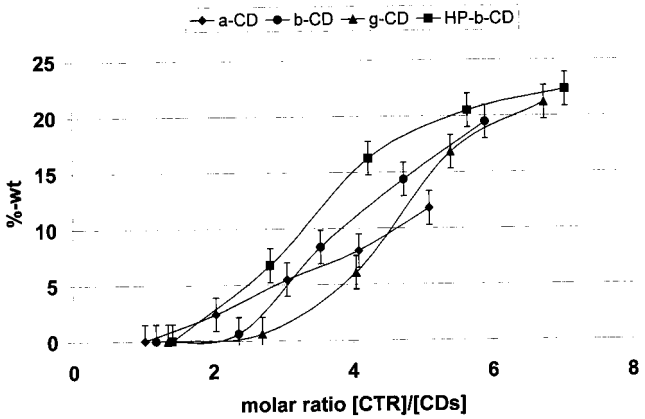


Figure 3. Influence of the molar ratio [CTR]/[CDs] in the impregnation solution. Curing: 5 min at 160 °C; 0 < [CTR] < 100 g/L; [NaH2PO2] = 10 g/L; [CDs] = 100 g/L.

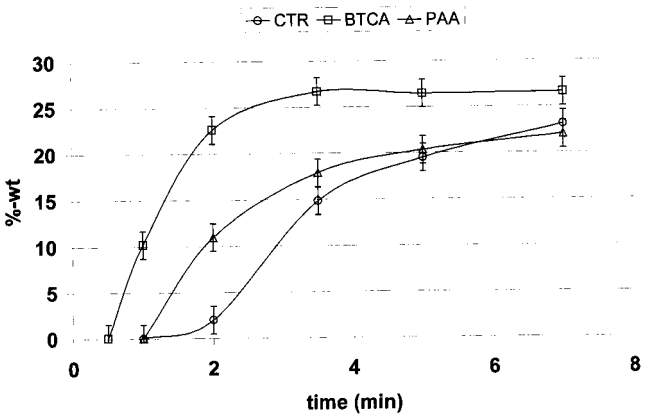


Figure 4. Kinetic study of the grafting reaction of β-CD with BTCA, PAA and CTR. Curing : 160 °C, [PCA] = 100 g/L; [NaH_2PO_2] = 10 g/L; [β-CD] = 100 g/L.

served that it was necessary to respect a threshold value of the [CTR]/[CDs] molar ratio in order to observe the permanent modification of the samples. It is also observed that the modification of the fibers occurred especially when the concentration in CTR was 1.5 to 5.5 times that of CDs and that a saturation phenomenon was obtained for an important excess of CTR.

These results reveal that below the threshold ratio, the crosslinking reaction is not extended enough to ensure the permanent grafting. In the present case, the low molecular copolymers of CDs were removed during the washing step. On the contrary, above this threshold value, the molar ratio [CTR]/[CDs] was sufficient to ensure a crosslinking reaction that drove to the permanent grafting of the CDs.

The present reaction was also extended to the use of BTCA and PAA, a tetra carboxylic and a polymeric polycarboxylic compound, respectively. As reported in Figure 4, the kinetic study showed that the reactivities of the three crosslinking agents varied in the order BTCA > PAA > CTR. For example, 10%-wt grafting rate were obtained within about 1, 2 and 3 min, with the three PCA respectively. So, as BTCA necessitates the lowest reaction time for attaining a definite grafting rate, it can be deduced that it has the best reactivity. This observation has been previously reported in the graft reaction of CDs onto natural fibers [10]. Furthermore, Welsh *et al.* obtained the same results in the study of the application of BTCA in the process of durable press finishing of cotton [14].

Conclusion

We previously observed that PCA were effective in the grafting reaction of CDs onto natural fibers that carry reactive chemical functions. This study showed the versatility of the present method whilst it is also applicable to a synthetic and neutral fiber as PET. This process requires a classical finishing equipment, the use of non toxic chemicals and does not involve any organic solvent. Furthermore, it is applicable to all types of CDs (as long as they carry enough OH groups). A recent application concerns the capture of fragrances (in their volatile form or in solution) and their prolonged and controlled release [15].

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