

# Mechanical and physico-chemical characterization of cyclodextrin finished polyamide fibers

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**Abstract** We present the study of the cyclodextrin (CDs) finishing of polyamide fibers (PA) by means of citric acid (CTR) as crosslinking agent. We observed that the mode of grafting happened by the formation of a crosslinked polymer formed between CTR and CDs. This polymer physically adhered to the fibers network and was resistant to hot water washings. Modified fibers were characterized by evaluating the contact angle with a polar liquid and by studying the hysteresis of damping of PA fibers (Cahn balance) with various grafting rates and by studying the absorptivity of grafted fabrics via the technique of the posed drop (Digidrop<sup>®</sup> instrument). Then a mechanical characterization of the PA fabrics grafted with various proportions of CDs was accomplished, by traction and tear tests by using a tensile-test bench Lohmery. Finally a topographic study of PA grafted surfaces was approached by atomic force microscopy (AFM and LFM; contact and non-contact mode) which permitted to evaluate the roughness and the chemical heterogeneity of the grafted surfaces.

**Keywords** Polyamid-6-6-fibers · Cyclodextrin · Citric acid · Textile finishing

## Introduction

The application of cyclodextrins (CDs) and their derivatives in the textile domain appeared in the early 80's [1]. The permanent binding of CDs onto textile fibers allowed that the properties of CDs became intrinsic to the modified fibers [2, 3], and gave rise to a new generation of *intelligent textiles* which presented enhanced capacities of sorption and delivery of active molecules.

In our laboratory we proposed a method for the grafting of CDs onto polypropylene nonwoven fabrics by using the electron beam technology [4, 5]. Then, we reported the possibility to graft CDs onto cotton and wool fibers by using polycarboxylic acids (PCA) as binding agents [6, 7]. More recently, we also reported that this method was also applicable to polyester fibers [8].

The current paper reports the modification of polyamide (PA) [9] made fabrics and emphasizes their physical and physico-chemical characterization. We illustrate the study of the parameters involved in this specific textile processing. These parameters include the curing conditions (temperature, time) and also the nature of the reactants. The last mentioned consist of citric acid (CTR) applied as crosslinking agent; sodium dihydrogen hypophosphite ( $\text{NaH}_2\text{PO}_2$ ) was used as catalyst,  $\beta$  and  $\gamma$ -CD and the two hydroxypropylated  $\beta$ -CD and  $\gamma$ -CD (HP- $\beta$ -CD and HP- $\gamma$ -CD, respectively) have been tested. Then, a mechanical and physico-chemical characterization was applied in order to

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define the presence and the effectiveness of the fiber coating.

## Materials and methods

Polyamide 6-6 (PA 6-6) woven fabric (surface 80 g/m<sup>2</sup>, wet pick up = 112 wt.%) was supplied by GEMTEX.  $\alpha$ -CD,  $\gamma$ -CD and hydroxypropylated  $\gamma$ -CD (HP- $\gamma$ -CD) were gifts from Wacker Fine Chemicals GmbH (Cavamax<sup>®</sup>, Burghausen, Germany).  $\beta$ -CD and Hydroxypropylated  $\beta$ -CD (HP- $\beta$ -CD) were gifts from Roquette (Kleptose<sup>®</sup>, Lestrem, France). Citric acid (CTR) and sodium dihydrogen hypophosphite were Aldrich chemicals (Milwaukee, WI, USA). The textile finishing equipment consisted of a padder and thermofixation oven (Minithermo<sup>®</sup>, Roaches Leek, UK). Fabric samples, were previously washed in order to eliminate the industrial finishing products and especially sizing. Fabrics were impregnated by the aqueous solution containing CD (100 g/l), CTR (100 g/l) and catalyst (10 g/l), roll-squeezed, dried and thermofixed (at variable temperatures and times) and finally washed several times with warm water. Raw and treated samples were dried 30 min at 104 °C before being weighted. The weight gain of the fabrics (symbolized by wt.%) was measured to evaluate the yield of the grafting reaction, and calculated by the following equation: wt.% =  $(m_f - m_i) / m_i \cdot 100$ . Where  $m_i$  and  $m_f$  were the weights of the samples before and after treatment, respectively. The precision on the weight gain measurements was  $\pm 1.5$  wt.%

The thermodynamic characteristics of the fibres were determined by measurements of contact angles with glycerol, that presents an energy of surface of 63,4 mJ/m<sup>2</sup>.

It is possible to evaluate the surface tension of a material through the contact angle measurement of various liquids of known surface energy. Thus, the weaker is the contact angle between the liquid and the substrate (in our case, a fiber), the higher is the damping.

The following formula is used:

$$\cos \theta = \frac{mg}{2\pi r_f \gamma}$$

where:  $\theta$ : angle of damping;  $\gamma$ : energy of surface of solvent;  $g$ : gravity;  $r_f$ : ray of fiber, measured under the microscope (for our case  $r_{f \text{ moy}} = 19.5 \mu\text{m}$ );  $m$ : mass of the fiber immersed into the liquid.

The mechanical properties of virgin and grafted fibers were studied by tensile-tests (NORM NF IN ISO

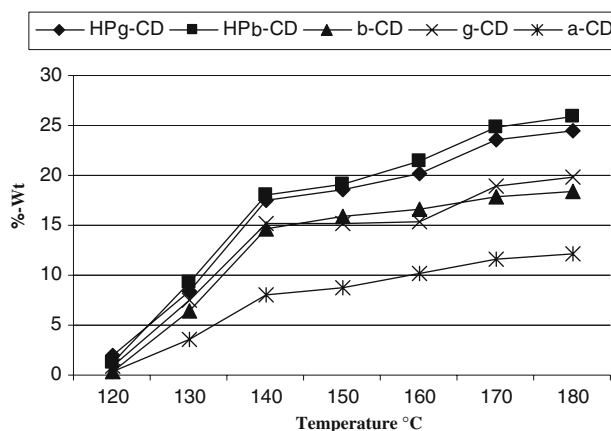
13 934-1). A tensile-testing instrument Adamel Lhomargy 2/M was used, the jaws were equipped with a system of tightening with constant pressure. A sensor of 10 kN was used. For our tests, a preload of 10 kN was imposed to the test pieces. The initial distance between the jaws was fixed to 20 mm, the speed of traction was fixed to 100 mm/min.

The tests of tear (NORM NF G 07.146) were carried out on a dynamometer (with a constant speed of displacement GAC). The initial distance between the jaws was 100 mm. The speed of traction was 100 mm/min, the length of the testing pieces was 200 mm, width 50 mm.

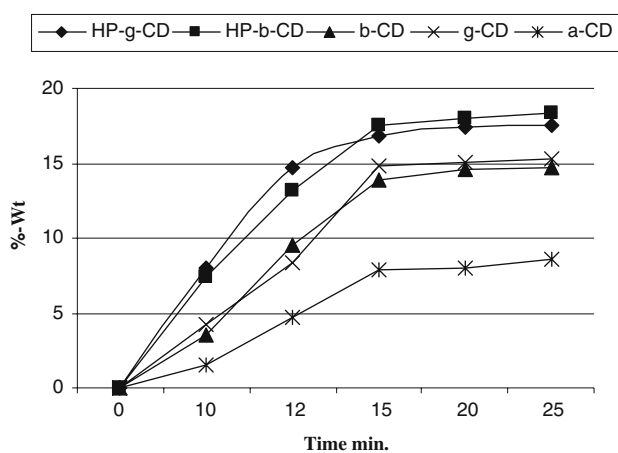
## Results and discussions

The treatment of PA fabrics by CTR and CDs resulted in a relative weight increase of the samples, depending from temperature and time of fixation as observed in Figs. 1 and 2, respectively. In Fig. 1, one can observe that the grafting rates of the treated samples progressively increased with temperature in the range 120–180 °C. The grafting rate sharply increased when the temperature was comprised between 125 and 140 °C, and still increased in a lesser extent up to 180 °C. The plateau value that corresponded to the maximal conversion of reactants preliminary impregnated onto the fabric. At 180 °C, grafting rates close to 25 wt.% were obtained in the case of HP- $\beta$ -CD and HP- $\gamma$ -CD, and 19 wt.% for the two natives  $\beta$ -CD and  $\gamma$ -CD. Whilst only 12 wt.% was reached in the case of the sample treated with  $\alpha$ -CD.

Figure 2 presents the time dependence of the reaction. At 140 °C, the grafting rate rapidly increased within the first 15 min of curing, and then a plateau was



**Fig. 1** Influence of the curing temperature on the grafting rate of the PA fabric samples. Time of curing 20 min



**Fig. 2** Influence of curing time on the grafting rate of the PA fabric samples. CTR as crosslinking agent. Temperature of curing: 140 °C

reached. As mentioned above, the highest grafting rates were observed on textiles finished with HP- $\beta$ -CD and HP- $\gamma$ -CD (17–18 wt.% after 20 min), 14–15 wt.% was observed in the cases of  $\beta$ -CD and  $\gamma$ -CD, while  $\alpha$ -CD presented a lesser effectiveness (8 wt.% after 20 min). We concluded that the number of glycosidic units per CD moiety and their partial substitution by hydroxypropyl groups were influent factors with regard to their reactivity towards the grafting reaction. On one hand, the reactivity of a CD unit depends from the number of OH groups available for the polyesterification (statistical factor), on the other hand, hydroxypropyl substituent groups offer hydroxyl functions with enhanced reactivity compared to OH groups present in the 2, 3 and 6 positions on the glucopyranosic units (sterical and reactivity factors).

As previously reported [9], the reaction happened through the polyesterification between CTR and CDs, to give rise to the formation of a crosslinked polymer (polyCTR-CD), which physically adhered to the fibers. This functionalization mode was resistant as we could observe no variation of the weight of the samples upon

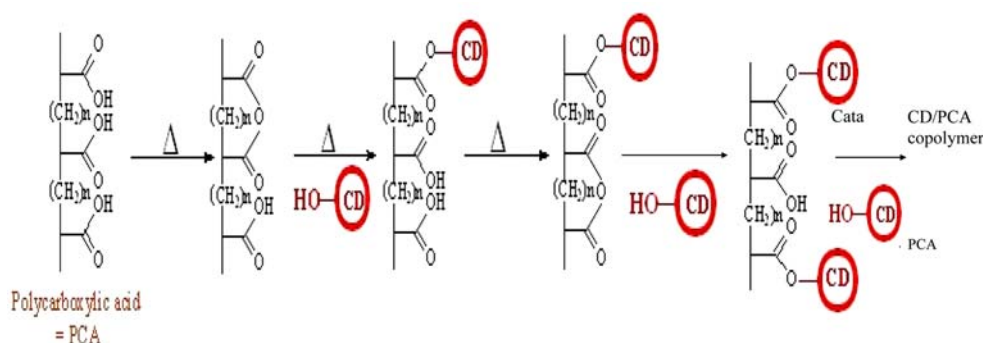
several washing cycles with hot water carried out with soxhlet extractors (Scheme 1).

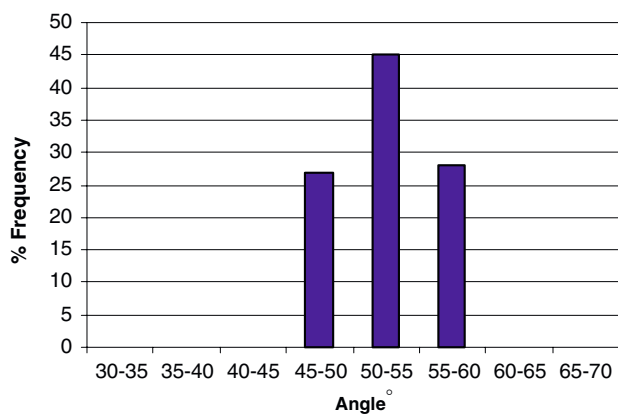
This permanent grafting was characterized by evaluating the contact angle of PA fibers grafted with different types of cyclodextrins, with glycerol, on a Cahn balance at various rates of grafting and by studying the absorptivity of grafted fabrics via the technique of the posed drop measured by Digidrop<sup>®</sup> instrument. All samples used in the following characterization tests were prepared by applying 140 °C and 20 min as curing parameters.

The grafting rate was varied by the dilution of the initial impregnation solution (CD/catalyst/CTR in water). So, all the samples of a series underwent the same grafting conditions.

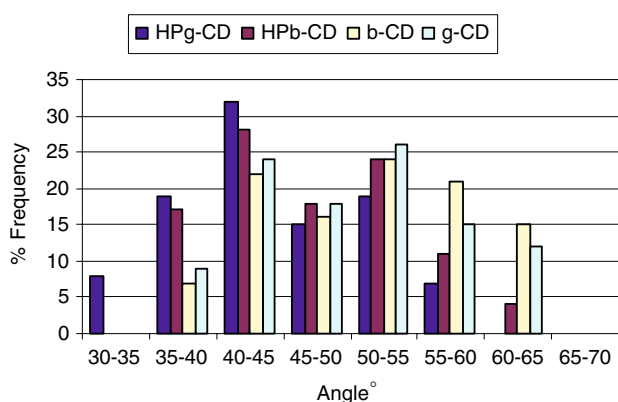
Figure 3 displays that the average wetting angle on virgin PA was 50–55°. Besides, Fig. 4 displays a double distribution around 50–55° (virgin PA surface) and 40–45° (polyCTR-CD covered surface) on samples with medium grafting rates. At last, Figure 5 shows a single distribution around 40–45° which indicates that for high grafting rates, most of the fibers surface was covered by the hydrophilic polyCTR-CD polymer. The hysteresis of damping reported in Fig. 6, displays the difference between the advancing contact angle (measured during the immersion of the fiber into the liquid test) and the receding contact angle (calculated after the emergence of the fiber). In the case of the control (ungrafted fiber), the hydrophobic surface caused an important hysteresis of damping. Firstly this value gently increased with the grafting rate, until 9 wt.%, then it rapidly decreased for increasing grafting rates. That means that, firstly, as the grafting rate increased, the heterogeneity of the fibers firstly increased (majority of PA surface) up to 9 wt.%. Secondly, the surface became more and more homogeneous (as polyCTR-CD covered most of the surface). As in the right part of the plot, fibers became more hydrophilic, the hysteresis of damping decreased.

**Scheme 1** Polymerisation reaction between PCA and CDs

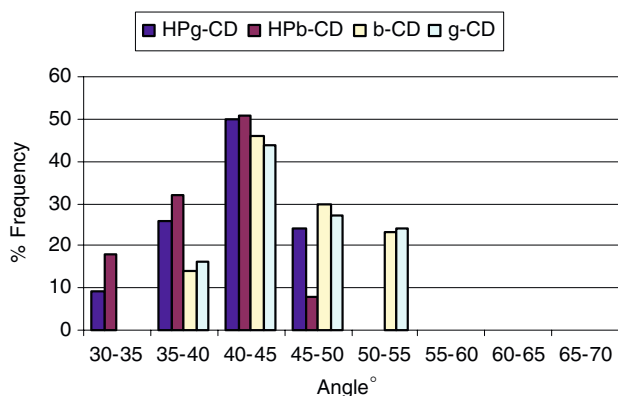




**Fig. 3** Distribution of wetting angles of non-treated PA fibers

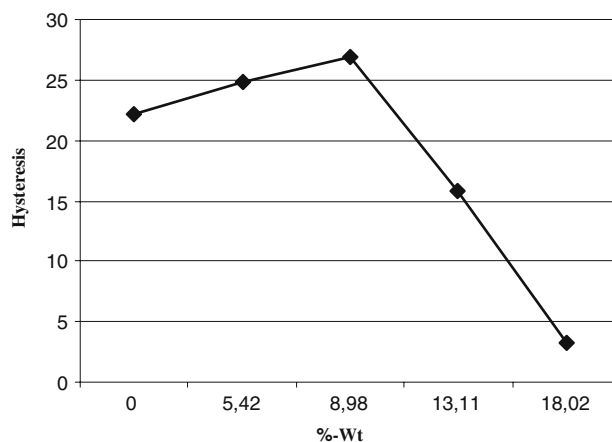


**Fig. 4** Distribution of wetting angles of PA fibers grafted with 6.5%, 7.3%, 9% and 9% of respectively;  $\beta$ ,  $\gamma$ , HP- $\beta$  and HP- $\gamma$ -CD

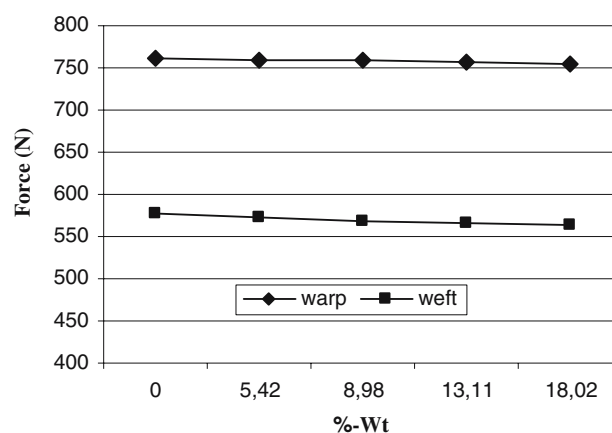


**Fig. 5** Distribution of wetting angles of PA fibers grafted with 14%, 15%, 18% and 17% of respectively;  $\beta$ ,  $\gamma$ , HP- $\beta$  and HP- $\gamma$ -CD

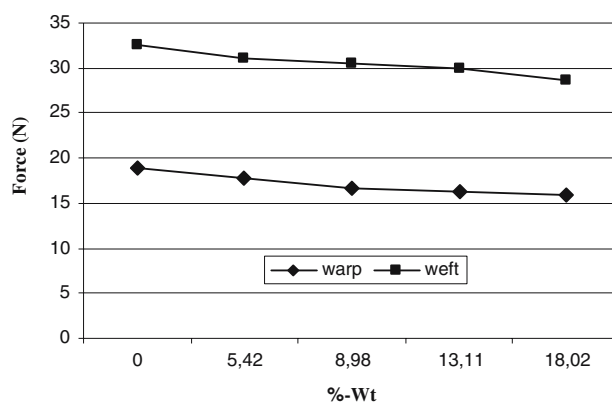
For the traction and tear tests reported in Figs. 7, 8 we noticed that at a temperature of curing of 140 °C during 20 min, the obtained results showed no modi-



**Fig. 6** Hysteresis of damping according to the rate grafted (curing 20 mn at 140 °C)



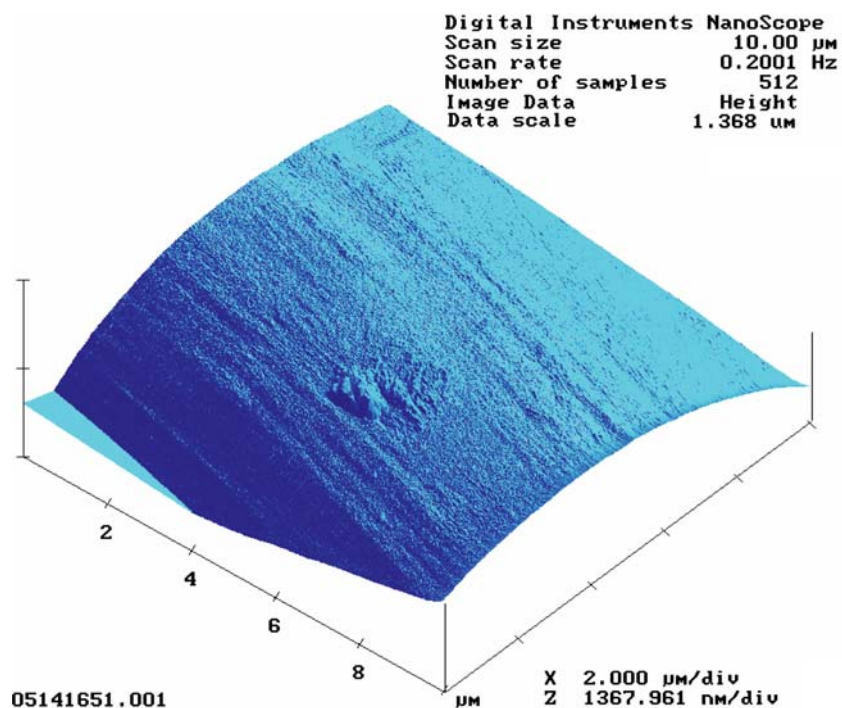
**Fig. 7** Force of rupture according to the grafted rate (curing 20 min at 140 °C)



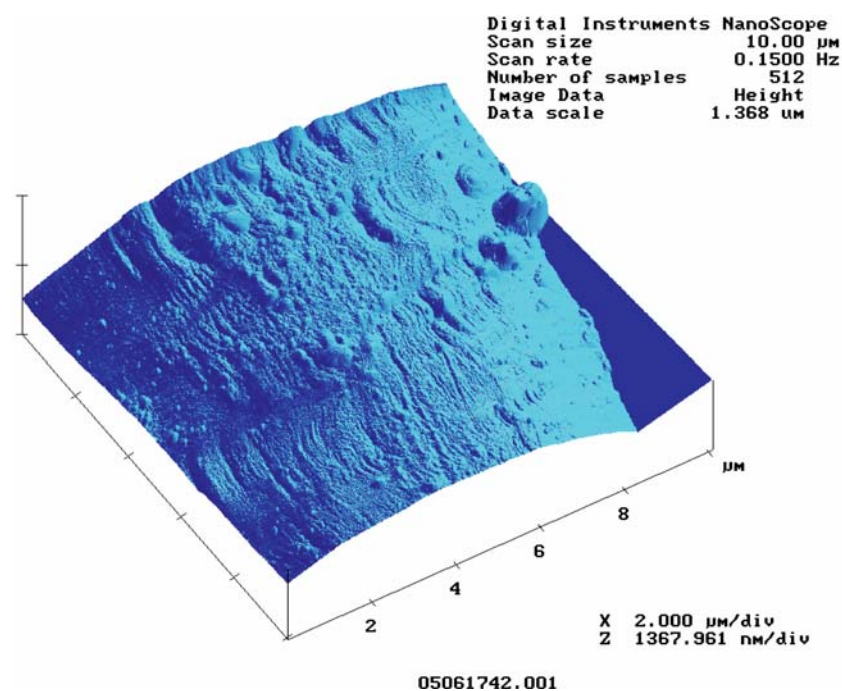
**Fig. 8** Force of tear according to the grafted rate (curing 20 min at 140 °C)

fication of the force of rupture neither of the average force of tear. So the grafting reaction respected the mechanical properties of the fabric.

**Fig. 9** Fiber of non-grafted PA observed in AFM



**Fig. 10** Fiber of grafted PA observed in AFM with 18 wt. %



In addition, a topographic study of PA grafted surfaces was approached by atomic force microscopy (AFM and LFM; contact and non-contact mode) which enabled us to evaluate the roughness and the chemical heterogeneity of grafted surfaces. As illustrated in Figs. 9, 10 we noticed a clear modification in the topography of surfaces of the grafted PA fibers. This reveals the presence of polyCTR-CD deposited on the surface.

## Conclusion

After the successful grafting of CDs onto natural fibers and polyester previously reported, this study shows the versatility of the present method whilst it is also applicable to polyamide fabrics. This process requires a classical textile finishing equipment, the use of non-toxic chemicals and does not involve any organic

solvent. Furthermore, it is applicable to all the members of the CD family.

By applying a temperature of grafting of 140 °C during 20 min, we could obtain a PA with an important grafting rate (18 wt.%). Though, grafting rates in a lesser extent (5 wt.%) were sufficient to improve the controlled release of antibiotics from modified fibres [10]. CD finished fibers presented an enhanced hydrophilicity and kept their initial mechanical properties. The AFM topographic study confirmed the presence of the graft.

The study of the various chemical and physical properties of surfaces of the PA grafted by cyclodextrins shows that this finishing will be able to attribute new properties to polyamide, by improving for example its dyeing affinity. Moreover, the contribution of cyclodextrins as a molecule able to complex a broad range of active biologically molecules, will open new opportunities in the field of high value added textiles (to be published).

## References

1. Szejtli, J., Zsádon, B., Fenyvesi, E., Horváth, O., Tudos, F.: US Patent 4,357,468 (1982)
2. Poulakis, K., Buschmann, H.J., Schollmeyer, E.: German Patent DE 40 35 378 A1 (1992)
3. Denter, U., Schollmeyer, E.: In: Szejtli, J., Szenté, L. (eds.) Proc. VIIIth Int. Cycl. Symp. Budapest, pp. 553–558. (1996)
4. Le Thuaud, P., Martel, B., Crini, G., Maschke, U., Coqueret, X., Morcellet, M.: Grafting of cyclodextrins onto polypropylene nonwoven fabrics for the manufacture of reactive filters-Part 1: synthesis parameters. *J. Appl. Polym. Sci.* **77**, 2118 (2000)
5. Weltrowski M., Martel B., Morcellet M.: Patent PCT 00378 (2000), US 09/913,448 (2001), CA 2,362,534 (2001)
6. Martel, B., Weltrowski, M., Ruffin, D., Morcellet, M.: Polycarboxylic acids as crosslinking agents for grafting cyclodextrins onto cotton or wool fabrics. *J. Appl. Polym. Sci.* **83**, 1449–1456 (2002)
7. Welsch, C.M.: Durable press finishing of cotton with polycarboxylic acids. *Text. Res. J.* **58**, 480 (1988)
8. Martel, B., Morcellet, M., Ruffin, D., Ducoroy, L., Weltrowski, M.: Finishing of polyester fabrics by cyclodextrins by using polycarboxylic acids as crosslinking agents. *J. Incl. Phenom. Macrocycl. Chem.* **44**, 443–446 (2002)
9. Elgoul, Y., Martel, B., Morcellet, M., Campagne, C., El Achari, A.: Finishing of polyamide fabrics with cyclodextrins-polycarboxylic acids polymers. In: Duchene, D. (ed.) Proc. XIIth Int. Cyclodextrins Symp., Montpellier, pp. 651–654, (2004)
10. Blanchemain, N., Haulon, S., Boschin, F., Marcon-Bachari, E., Traisnel, M., Morcellet, M., Hildebrand, H.F., Martel, B.: Vascular Prostheses with controlled release of antibiotics-Part 1: surface modifications with cyclodextrin of PET vascular prostheses. *Biomol. Eng.* (2006, in press)