

# Polypropylene Biomaterial Grafted with Cyclodextrins and BTCA Acid as Crosslinking Agent

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**Abstract:** This study describes the use of cyclodextrin (CDs) as a finishing agent of polypropylene biomaterial (PP) by means of 1,2,3,4-butanetetracarboxylic acid (BTCA) as crosslinking agent. Grafting happened by the formation of a crosslinked polymer formed between BTCA and CDs. This polymer physically adhered to the fibers network and was resistant to hot water washings. We study the influence of parameters involved in this specific textile processing. These parameters include the curing conditions (temperature, time) and also the nature of the reactants which are 1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid (CTR) and polyacrylic acid (PAA), applied as crosslinking agents. Modified PP fibers were then characterized by evaluating the contact angle with a polar liquid and by studying the hysteresis of damping of PP fibers (Cahn balance) with various grafting rates. Infrared spectroscopy (ATR) and morphological (SEM) studies displayed the presence of the crosslinked CD polymer that coated the fibers, and permitted to evaluate the chemical heterogeneity of the grafted surfaces. A mechanical characterization of the PP fabrics grafted with various proportions of CDs was accomplished, by traction via a tensile-test. Finally a topographic study of PP grafted surfaces was approached by atomic force microscopy (AFM) which permitted to evaluate the roughness and the chemical heterogeneity of the grafted surfaces.

**Keywords:** Polypropylene, Fibers, Cyclodextrin Polymer, BTCA Acid, Grafting

## 1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides commonly composed of six, seven or eight alpha-D-glucose units ( $\alpha$ ,  $\beta$  and  $\gamma$  respectively) which have an overall shape reminiscent of a truncated cone. On account of their relatively hydrophobic interior cavity, CDs have the ability to form inclusion complexes with a wide range of substrates in aqueous solution. This property of CDs has led to their application in areas as varied as enzyme mimics, catalysis and the encapsulation of active substances, such as flavoring agents, fragrances, pesticides or drugs [1-2-3-4-5].

For these reasons the application of cyclodextrins and their derivatives in textile domain appeared since the early 80's. The permanent binding of CDs onto textile fibers presents 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 [6]. Besides, Denter et

al. [7] and Poulakis et al. [8] fixed a monochlorotriazinyl  $\beta$ -CD derivative onto different polymer materials including cotton fibers.

In 2000, Thuaut et al. proposed a method for the grafting of CDs onto polypropylene nonwoven fabrics by using the electron beam pre-irradiation method [9]. Then, Martel et al. reported the possibility to graft CDs onto cotton and wool fibers by using citric acid (CTR) as binding agents [10].

Then EL GHOUL et al. reported that this chemical path was also applicable to polyamide fibers, through the formation of a non covalently bound polymer that forms a coating around the fibers, made of cyclodextrins crosslinked with CTR [11].

Applications of these fibers finished with cyclodextrins concerned the release of fragrances [14], insect control agents, and our most application field investigated in the recent years concerned the antibiotic release from textile biomaterial devices applicable in vascular [15,16,17], periododental [18], and visceral surgery [19].

The current paper reports the modification of polypropylene (PP) made fabrics and emphasizes their physical and physicochemical 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 1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid (CTR) and polyacrylic acid (PAA), applied as crosslinking agents. 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. After, a mechanical and physico-chemical characterization was applied in order to define the presence and the effectiveness of the fiber coating.

## 2. Materials and Methods

Polypropylene samples used in this study were knitted fabrics of 12 threads/cm and having a surface weight of 400 g/m<sup>2</sup>.  $\beta$ -CD and Hydroxypropylated  $\beta$ -CD (HP- $\beta$ -CD) were purchased from Roquette (Kleptose R HPB, Lestrem, France).  $\gamma$ -CD and hydroxypropylated  $\gamma$ -CD (HP- $\gamma$ -CD) were purchased from Wacker Fine Chemicals (Burghausen, Germany). 1,2,3,4-Butanetetracarboxylic acid (BTCA), Citric acid (CTR), polyacrylic acid (PAA) and sodium dihydrogen hypophosphite were Aldrich chemicals (Saint Quentin Fallavier, France). The textile finishing equipment consisted of a padder and thermofixation oven (Minithermo®, 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 (100g/L), BTCA (100g/L) and catalyst (10g/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 and cooled down in a dessicator during 30 minutes before being weighed. The weight gain of the fabrics (symbolized by %wt) was measured to evaluate the yield of the functionalizing reaction, and calculated by the following equation: %wt =  $(m_f - m_i)/m_i \times 100$ . Were  $m_i$  and  $m_f$  were the weights of the samples before and after treatment, respectively.

The surface characteristics of the fibers were determined by measurements of contact angles with glycerol that presents a surface tension of 63,4 mJ/m<sup>2</sup>.

It was possible to evaluate the surface tension through the contact angle measurement of various liquids of known surface energy. Thus, the weaker was the contact angle between the liquid and the substrate (in our case, a fiber), the higher was the damping. The following formula (Eq.1) was used:

$$\cos \theta = \frac{mg}{2\pi Rf\gamma} \quad (\text{Eq.1})$$

Where  $\theta$  is contact angle,  $\gamma$  the surface energy of the

solvent,  $g$  is gravity,  $m$  is the weight of the fiber and  $R_f$  is the radius of the fiber section. In the present case,  $R_{f\text{moy}} = 38,5 \mu\text{m}$ .

From the curves illustrating the mass of liquid test moved by PP fiber, according to the depth of immersion, the contact angles were so calculated.

The morphological study was accomplished by a scanning electron microscope (SEM) GEMINI Ultra TM 55. The metallization of the PP samples was made via an apparatus Denton Vacuum Desk IV with a fine layer of gold. In order to obtain a homogeneous metallization for comparable results, all the samples were metalized at the same time, under the same conditions. The evaluation of the diameters of grafted fibers and the layer of the polyBTCA-CD caused by the grafting was given thanks to a software Smart-tiff accompanying the software of image processing by the machine.

The mechanical properties of virgin and grafted fibers were studied by tensile tests (NORM NF IN ISO 13 934-1). A tensile testing machine Adamel Lhomargy 2/M was used. The jaws of this machine were equipped with a system of tightening with constant pressure. A sensor of 10 N was used. For our tests, a preload force of 10 N was imposed to the test pieces. The distance between the jaws was fixed to 40 mm, the speed of traction was fixed to 100 mm/min.

## 3. Results and Discussion

The treatment of PP fabrics by BTCA and native or hydroxypropylated CDs resulted in the weight increase of the samples, depending from temperature and time of thermofixation as observed in Figures 1 and 2, respectively. In Figure 1, one can observe that the grafting rates of the treated samples gradually increased with temperature in the range 110 - 150 °C. The modification rate increased in a greater extent in the range 110°C-130°C and gently increased from 130 to 140°C and then reached a plateau value that corresponded to the maximal conversion of reactants preliminary impregnated onto the fabric. At 150°C, grafting rates close to 36%-wt were obtained in the case of HP- $\beta$ -CD and HP- $\gamma$ -CD, and 32%-wt for the two native  $\beta$ -CD and  $\gamma$ -CD [20].

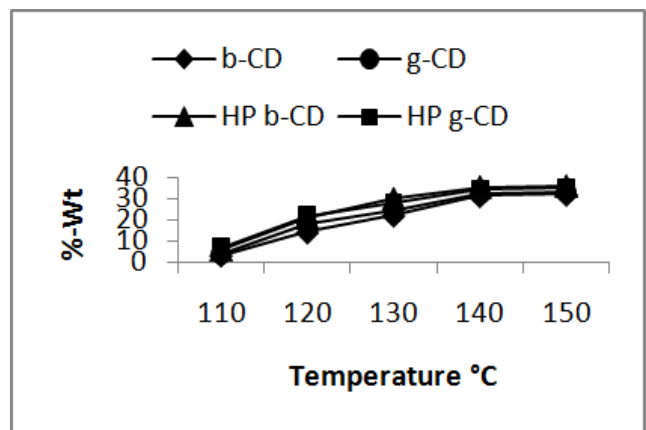


Fig. 1. Influence of the curing temperature on the modification rate of the PP fabric samples

In Figure 2, illustrating the time dependence of the grafting rate for PP fabric, we observed that the grafting rates of the treated samples progressively increased with time of curing. At a fixed temperature of 140°C, the grafting rates sharply increased within the first 8 minutes of curing and plateau values of the grafting rates was reached after 15 minutes. After 20 minutes, grafting rates closed to 34%-wt obtained in the case of HP-β-CD and HP-γ-CD, and 31%-wt for the two natives β-CD and γ-CD.

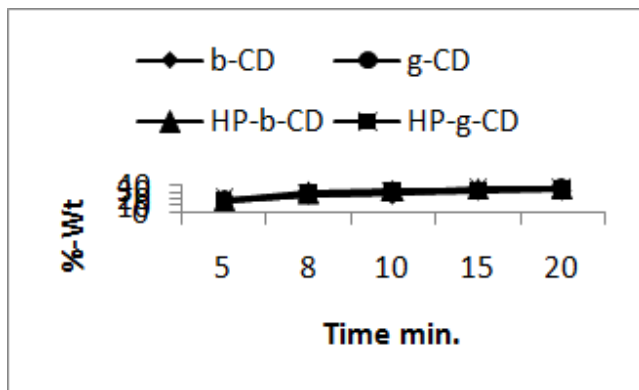


Fig. 2. Influence of the curing time on the modification rate of the PP fabric samples

So, this study showed that the grafting of the textile PP support occurred upon a threshold temperature of 120°C. Though, the aspect of the modified support was modified when a temperature above 145°C was applied (shrinking); therefore 140°C was chosen as the best compromise. At this temperature, the optimal grafting rate was reached within 15 minutes of thermofixation without degradation of the support. The deposition rate of the crosslinked CD polymer was more favourable in the case of the hydroxypropyl derivatives (HP-CDs) compared to the native varieties. It was also observed that HP-CDs were fixed at an inferior temperature than native CDs. The hydroxypropyl groups in 2 and 6 position of the glycosidic units can be considered as spacers that favorize the polyesterification reaction as illustrated by the figure 3 below:

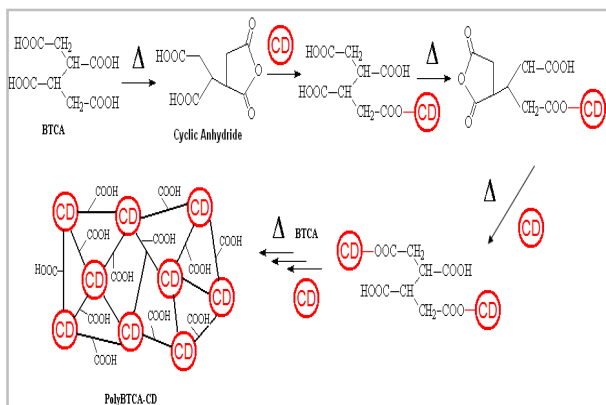


Fig. 3. Polymerization reaction between BTCA and CDs

To study the influence of the nature of the crosslinking agent we have tried two other polycarboxylic acids CTR and

PAA as crosslinking agents and we have compared their effectiveness in term of grafting rate to BTCA. The study was realised with the β-CD and the curing temperature was fixed to 140 °C.

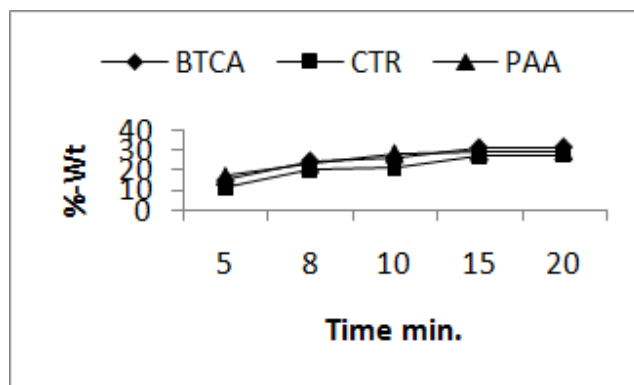


Fig. 4. Modification rate of the PP fabric samples finished with β-CD, according to the curing time

We noted in Figure 4 that for the three different types of polycarboxylic acids the grafting rates increased according to the curing time. The BTCA generally has the best results of grafting. The PAA required less time of curing before reaching a plateau value of the grafting rates after 10 minutes, while the other two polyacids reached a plateau value after 15 minutes of curing treatment. This permanent grafting was then characterized by evaluating the contact angle of PP fibers grafted with different types of cyclodextrins at various rates of grafting, on a Cahn balance, using glycerol as wetting liquid. All the samples finished with CD used for the characterisation tests were cured at 140°C during 20 minutes. In order to obtain samples with variable rates of grafting, we varied the dilution of the initial impregnation solution (CD/catalyst/BTCA) [21]. According to this experimental approach, the control of these parameters allowed us to obtain PP samples with grafting rates comprised between 0 and 31%-wt could.

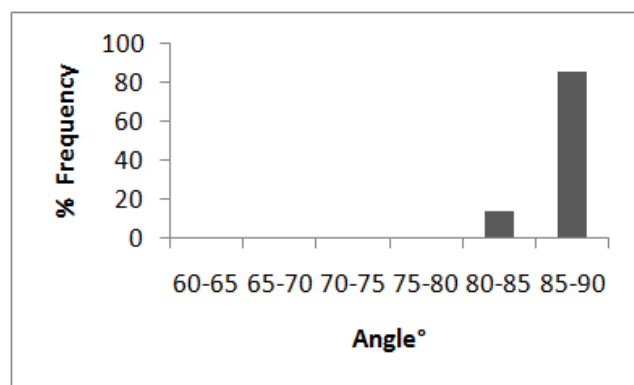
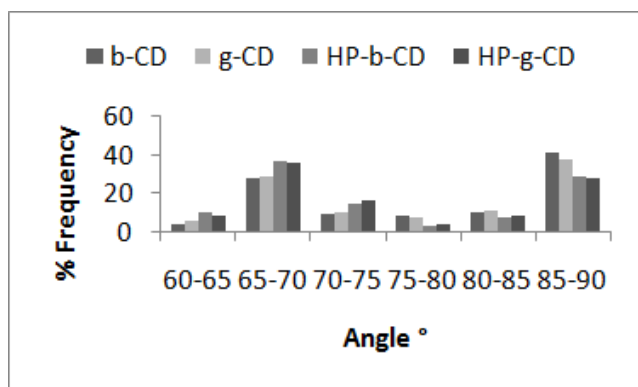
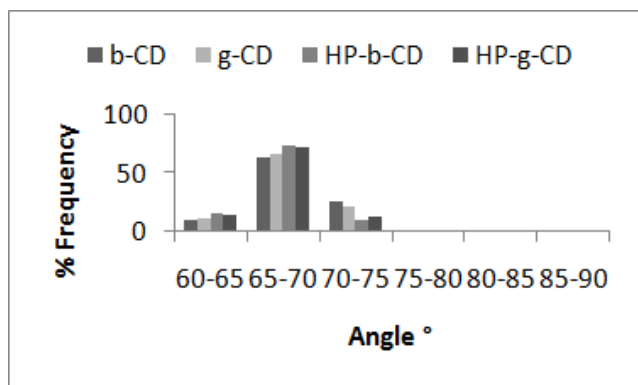


Fig. 5. Distribution of wetting angles of virgin PP fiber

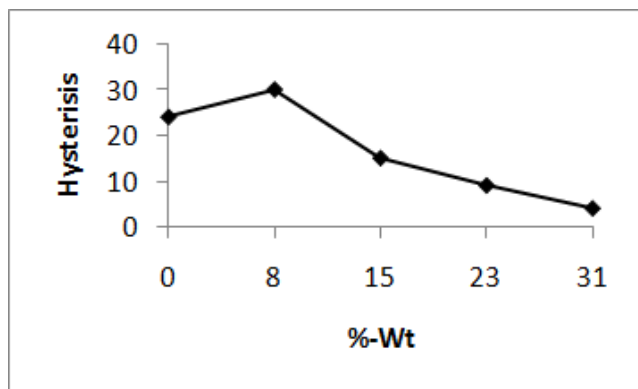


**Fig. 6.** Distribution of wetting angles of PP fibers grafted With  $\beta$ ,  $\gamma$  HP- $\beta$  and HP- $\gamma$ -CD (%Wt = 15)



**Fig. 7.** Distribution of wetting angles of PP fibers grafted With  $\beta$ ,  $\gamma$  HP- $\beta$  and HP- $\gamma$ -CD (%Wt = 31)

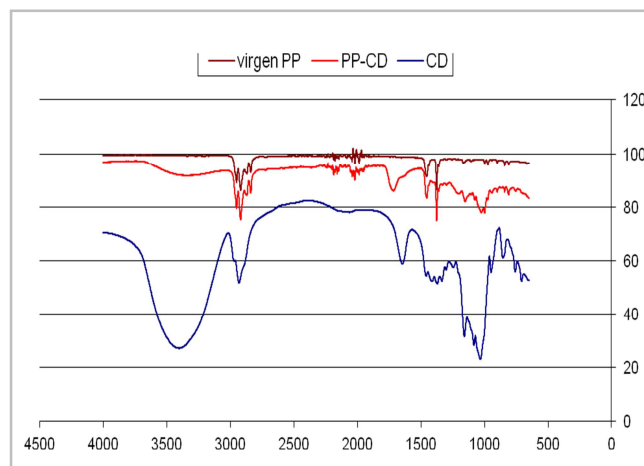
Histograms in Figures 5, 6 and 7 report that the contact angles decreased with the increase of the amount of fixed CDs. So, the wettability of the treated PP, increased with the grafting rate, and this was true for all the types of CDs used. In the same way a chemical homogenisation of surfaces sufficiently grafted lowered progressively the range of the wetting angles. This confirmed that, these surfaces became more covered by the polyBTCA-CD polymer.



**Fig. 8.** Hysteresis of damping according to the grafting rate of PP fabrics finished with polyBTCA- $\beta$ -CD

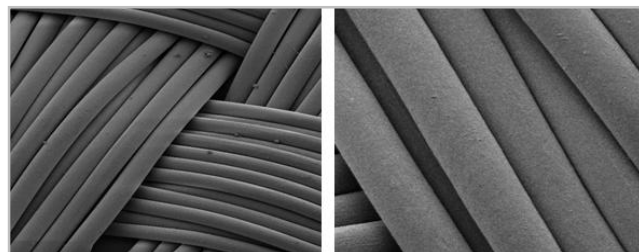
The hysteresis of damping reported in Figure 8, displays the difference between the advancing contact angle (obtaining during the immersion of the fiber into the liquid

test) and the receding contact angle (calculated after the emergence of the fiber). In the case of the control (virgin fiber), the hydrophobic surface caused an important hysteresis of damping. Firstly this value gently increased with the grafting rate, until 8%-wt, then it rapidly decreased for increasing grafting rates. That means that as the grafting rate increased, the heterogeneity of the fibers firstly increased (majority of PP surface) up to 8%, then decreased (polyBTCA-CD covered most of the surface). As in the right part of the plot, fibers became more hydrophilic, the hysteresis of damping decreased.



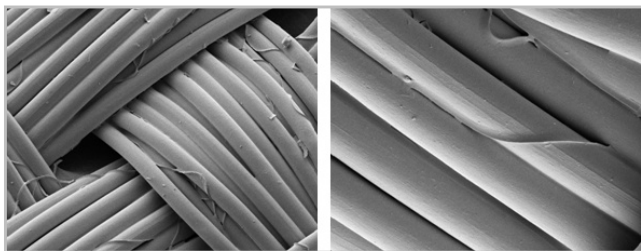
**Fig. 9.** IR Spectrum of virgin and polyBTCA- $\beta$ -CD grafted PP fabrics

The Figure 9 illustrated the IR spectrum of the virgin PP, superposed with those of the PP grafted by CDs and the poly-BTCA-CD. On the spectrum of the grafted PP a wide strip to  $3400\text{ cm}^{-1}$  appeared, corresponding to hydroxyl functions OH of CD and carboxylic acid functions COOH of the polyBTCA-CD. At a wavelength of  $1740\text{ cm}^{-1}$  appeared clearly the esters functions of the polyBTCA-CD. The band etheroxyde to  $1050\text{ cm}^{-1}$  of CD, was well appearing on the spectrum of the treated PP. The analyze of these various IR spectra, showed well the appearance of the peaks relative to our grafting, the polyBTCA-CD, on the spectrum of the PP grafted by CDs. This confirmed so well the presence of the polymer of cyclodextrins deposited on the surface of the PP fabric.



**Fig. 10.** SEM pictures of virgin PP fibers

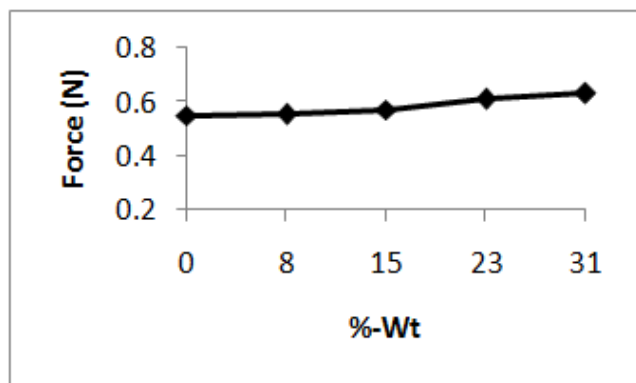




**Fig. 11.** SEM pictures of polyBTCA-β-CD grafted PP fibers (23%-wt)

The scan electronic microscopy enabled us to observe the surface of PP samples before and after grafting by CDs. The comparison of various micrographics showed a clear difference of the surface aspect of virgin and grafted fibers. On the virgin samples we noticed a regular surface but having in his texture a fine grit (Figure 10). On micrographics of the grafted samples (Figure 11) we observed a change of the surface quality of the grafted fibers that presenting a more uniform texture. The grafting with CDs was perfectly visible when the CDs form a regular polymer deposited on PP surface which coating fibers and connecting them in a uniform way. The empty spaces observed between virgin fibers were filled by the presence of the polymer, which coated fibers. One could observe that the grafting occurred well only on the scale of fibers without affecting the spaces between yarns, which remained completely distinct. One could also stress that the grafting occurred only by coating with any cluster of polyBTCA-CD imprisoned in the network of yarns. This observation means well that the grafting respects the porosity of the textile, without clogging the interstices between PP yarns.

A statistical study undertaken with an average of 20 virgin and grafted samples showed that the diameter of PP treated fibers increased approximately with 8 μm. This means that the layer of polyBTCA-CD would have a thickness of 4 μm.

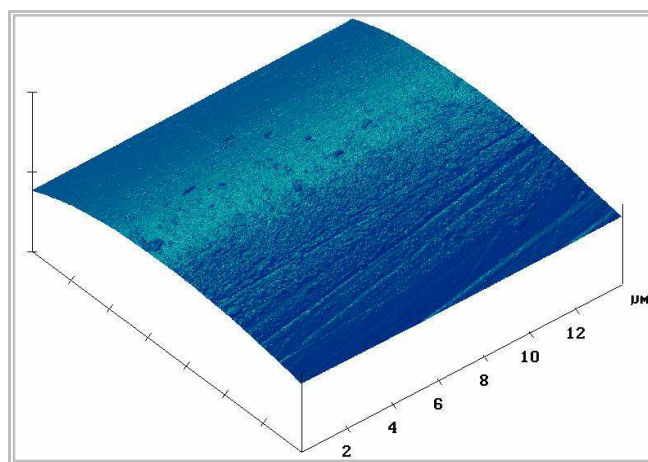


**Fig. 12.** Rupture force according to the grafting rate of PP fibers with polyBTCA-β-CD

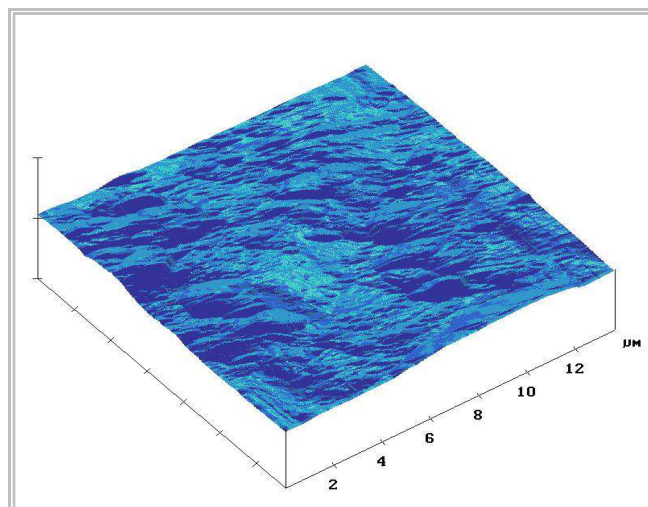
For the mechanical tests reported in Figure 12 we noticed that at a temperature of curing of 140°C during 20 minutes, the results obtained showed an increasing of the force of rupture. So the grafting reaction respected and more enhanced the mechanical properties of the grafted fabric.

In addition, a topographic study of PP grafted surfaces was

approached by atomic force microscopy (AFM with non-contact mode) which enabled us to evaluate the roughness and the chemical heterogeneity of grafted surfaces. As illustrated in figures 13 and 14 we noticed a clear modification in the topography of surfaces of the grafted PP fibers. This revealed the presence of polymer of CDs deposited on the surface. This modification increased with the time and the temperature of curing, which proved that the rate of covering surfaces increased with the grafting rate of CDs.



**Fig. 13.** AFM image of virgin PP fiber



**Fig. 14.** AFM Image of polyBTCA-β-CD grafted PP fiber (23%-Wt)

## 4. Conclusion

This study showed the effectiveness of the grafting of PP fabric in presence of BTCA as crosslinking agent. Furthermore, it was applicable to all the members of the CD family, native and modified CDs. By applying a temperature of grafting of 140°C during 20 minutes, we could obtain a PP sufficiently grafted (30%) with an enhanced hydrophilicity and without affecting the mechanical properties of the grafted fabrics.

The morphological study by SEM, involved the mode of covering by the polymer of CDs and showed that the CD

grafting respected the porosity of the PP treated fabrics. The AFM topographic and the infrared studies confirmed the presence of the polyBTCA-CD and the permanence of our grafting that resisted to severe washing cycles.

The study of the various chemical and physical properties of surfaces of the PP grafted with cyclodextrins showed that this finishing in presence of BTCA would be able to bring new properties to polypropylene, 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.

## References

- [1] H. Dodzuik (2006), ed. Wiley-VCH, Cyclodextrins and their complexes, Weinheim, ISBN 3-527-31280-3.
- [2] S. M. Gawish, S. R. Matthews, D. M. Wafa, F. Breidt, and M. A. Bourham (2007), *J. Appl. Polym. Sci.*, Vol. 103, p. 1900.
- [3] S. Salmaso, A. Semenzato, P. Caliceti, Johan, H. Sonvico, C. Dubernet, P. Couvreur (2004), *Bioconjugate Chem.*, 15 (5), p. 997.
- [4] T. Loftsson, D. Duchêne (2007), *International Journal of Pharmaceutics*, 329, 1.
- [5] R. Breslow, S. D. Dong (1998), Biomimetic reactions catalysed by cyclodextrins and their derivatives. *Chem. Rev.* 98, 1997-2012.
- [6] J. Szejtli, B. Zsádon, E. Fenyvesi, O. Horváth, and F. Tudos (1982), US Patent 4, 357, 468.
- [7] K. Poulakis, H.J. Buschmann, and E. Schollmeyer (1992), German Patent DE 40 35 378 A1.
- [8] U. Denter and E. Schollmeyer: in J. Szejtli and L. Szente (1996), *Proc. VIII<sup>th</sup> Int. Cycl. Symp. Budapest*, pp. 553-558.
- [9] P. Le Thuaud, B. Martel, G. Crini, U. Maschke, X. Coqueret and M. Morcellet (2000), *J. Appl. Polym. Sci.*, 77, 2118.
- [10] B. Martel, M. Weltrowski, D. Ruffin, and M. Morcellet (2002), *J. Appl. Polym. Sci.*, 83, 1449.
- [11] Y. El Ghoul, B. Martel, M. Morcellet, C. Campagne, A. El Achari, and S. Roudesli (2007), *J. Incl. Phenom. Macrocycl. Chem.*, 57, 47.
- [12] M. Weltrowski, M. Morcellet, and B. Martel, FR 9901967 (2000), DE 600 10 055 T2 (2005), EP 1,157,156 B1 (2004); US 7,048,769B1 (2006), CA 2,362,534, WO 0047811.
- [13] B. Martel, D. Ruffin, J. M. Hougard, and M. Morcellet (2004), *Proc. XII<sup>th</sup> International Cyclodextrin Symposium*, Montpellier, May 16-19, 639.
- [14] N. Blanchemain, S. Haulon, B. Martel, M. Traisnel, M. Morcellet, and H. F. Hildebrand (2005), *Eur. J. Vasc. Endovasc. Surg.* 29, 628.
- [15] M. Weltrowski, B. Martel, and M. Morcellet (2001), Patent PCT 00378 (2000), US 09/913,448 (2001), CA 2,362,534.
- [16] N. Blanchemain, T. Laurent, F. Chai, C. Neut, S. Haulon, V. Krump-Konvalinkova, M. Morcellet, B. Martel, C. J. Kirkpatrick, and H. F. Hildebrand (2008), *Acta Biomaterialia* 4, 1725.
- [17] F. Boschini, N. Blanchemain, M. Bria, E. Delcourt-Debruyne, M. Morcellet, and H. F. Hildebrand (2006), *J. of Biomed. Mater. Res.: Part A.*, 79, 78.
- [18] Y. El Ghoul, N. Blanchemain, C. Campagne, A. El Achari, S. Roudesli, M. Morcellet, B. Martel, and H. F. Hildebrand (2008), *Acta Biomaterialia*, 4, 1392.
- [19] Y. El Ghoul, B. Martel, A. El Achari, C. Campagne, L. Razafimahefa, and I. Vroman (2010), *Polymer Journal* 42, 804.