Grafting of Cyclodextrins onto Polypropylene Nonwoven Fabrics for the Manufacture of Reactive Filters. II. Characterization

BERNARD MARTEL,[1] PHILIPPE LE THUAUT,[1] GREGORIO CRINI,[2] MICHEL MORCELLET,[1] ANNA-MARIA NAGGI,[3] ULRICH MASCHKE,[1] SABRINA BERTINI,[3] CARMEN VECCHI,[4] XAVIER COQUERET,[1] GIANGIACOMO TORRI[3]

[1] Laboratoire de Chimie Macromoléculaire, UPRESA CNRS 8009, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France

[2] Université de Franche Comté, Centre de spectrométrie, Route de Gray, La Bouloie, 25030 Besançon, France

[3] Istituto Scientifico di Chimica et Biochimica "G. Ronzoni," 81 Via G. Colombo, 20133 Milano, Italy

[4] Stazione Sperimentale per i Combustibili, 3, Viale De Gasperi, 20097 San Donato Milanese, Italy

Received 29 November 1999; accepted 15 March 2000

ABSTRACT: A novel method for the preparation of immobilized α, β, or γ-cyclodextrins on polypropylene nonwoven supports has been previously presented. The obtained new materials were prepared by graft-polymerization of glycidyl methacrylate onto polypropylene after activation of the support by the electron beam technique, followed by the coupling of cyclodextrins with the epoxide groups. The structure of the resulting materials is characterized in detail using Fourier transform infrared spectroscopy, solid state nuclear magnetic resonance analysis, differential scanning calorimetry, thermogravimetric analysis, and optical microscopy. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2166–2173, 2000

Key words: cyclodextrin; polypropylene; grafting; electron beam; nonwoven; filter

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides whose main representatives consist of six to eight glucopyranose units called α-, β-, and γ-CD, respectively. Their specific shape is responsible for their original properties that consist of the possibility for organic substrates to penetrate spontaneously and reversibly inside their central cavity.[1] Therefore, molecules such as fragrances,[2] drugs,[3] pesticides,[4] and textile dyestuffs[5,6] can be complexed by CDs. The main interests of complexation by CDs are: 1. physico-chemical stabilization; 2. improvement of water solubility; and 3. reduction of the volatility of the substrate. The immobilization of CDs as insoluble materials leads to materials that can be used as sorbents for the decontamination of waste waters.[6] Le Thuaut et al.[7] have recently reported a new way of immobilization of CDs onto polypropylene (PP) nonwoven fabrics particularly adapted for filtration processes.

The functionalization of textile supports by CDs is a challenge that has been investigated in the last decade. The permanent fixation of CDs onto fibers allows preservation of the presence and the specific properties of the former along the successive washing cycles. The main purpose con-

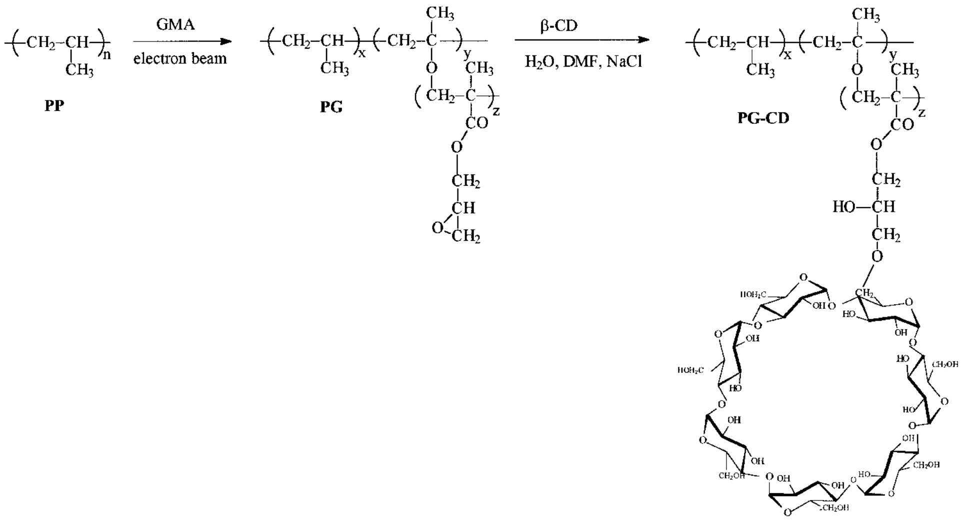
---

Correspondence to: B. Martel. E-mail: bernard.martel@univ-lillel.fr

Contract grant sponsor: European Union through the FAIR program; contract grant number: CT 95 0300.

Contract grant sponsors: Région Nord Pas-de-Calais, ADEME and the E. U. FEDER program.

Journal of Applied Polymer Science, Vol. 78, 2166–2173 (2000)



Scheme 1

sists in grafting CDs without any deterioration of their complexing ability. Several interesting approaches in the textile functionalization by CDs have been reported by Schollmeyer et al.[8–10] and Reuscher et al.[11,12] However, these processes do not include PP textile supports.

Our method of immobilization of CDs onto PP consists of two steps. The PP is first submitted to electron beam irradiation, followed by the graft polymerization of glycidyl methacrylate (GMA). A nonwoven PP carrying polymerized GMA (called PG) was the intermediate product. In a second step, the epoxide groups of PG react with CDs' molecules to create the covalent linkage of the former, leading to the final product that we called PG-CD.[7]

In this report, the characterization of this new kind of textile materials is presented. Fourier transform infrared (FTIR) spectroscopy, solid state nuclear magnetic resonance (NMR) analysis, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and optical microscopy have been used as analytical techniques. As in the solid state, the differentiation between α, β, or γ PG-CD cannot be achieved; the following results only concern β-CD functionalized supports.

EXPERIMENTAL

Materials

The needled nonwoven PP was 2-mm thick and had a surface weight of 100 g/m^2 (donation from Texel Inc., Saint Elzear de Besuce, Canada). The lubricant was previously removed by Soxhlet extraction.

The GMA monomer (Acros, Gael, Belgium) was used without purification. α-, β-, and γ-CDs of analytical grade were supplied by Wacker GmbH, Munich, Germany. All other chemicals were of analytical reagent grade.

The synthesis of the CD-PP (PG-CD) supports has been described in the first part of this study.[7] It follows the reaction scheme described in Scheme 1. The content of GMA in the intermediate and final filters (PG and PG-CD) is expressed as the weight increase of the initial PP upon graft polymerization of GMA (GMA wt %). The quantity of grafted β-CD was also measured by the gravimetric method and is expressed in μmol of β-CD per gram of final support.

Analytical Procedures

Infrared spectra were recorded with a Perkin-Elmer FTIR 2000 System using the diffuse reflectance equipment combined with a conventional TGS detector.

Solid state ^{13}C-NMR techniques like cross polarization magic angle spinning (CPMAS) and MAS were used for the characterization of the PG and PG-CD supports. The spectra were recorded with a Bruker CXP-300 or ASX 300 spectrometer operating at 75.47 MHz. Details of the NMR solid state conditions have already been reported.[13]

TGA was performed under air flow using a Shimadzu TGA 51 instrument. Temperature program: 10°C/min from ambient to 650°C.

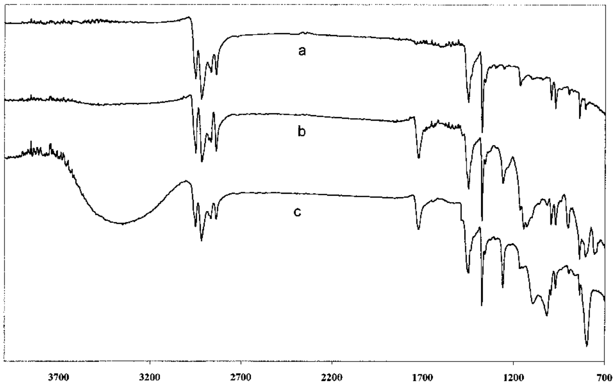


Figure 1 FTIR-ATR spectra of (a) PP; (b) GMA-grafted PP (GMA = 96 wt %); and (c) GMA-grafted PP after immobilization of β-CD (130 μmoles/g of CD).

A Perkin-Elmer DSC 7 instrument was used for the DSC measurements. Temperature program: hold for 3 min at 70°C and further heat to 195°C with a gradient of 10°C/min. The sample holder was a hermetically sealed aluminum container.

The investigation of the materials by optical microscopy was performed with an OLYMPUS BHS microscope equipped with a camera.

RESULTS AND DISCUSSION

The ATR infrared spectra of the materials obtained after each reaction step of the synthesis are presented in Figure 1. The spectrum of PG (b), compared with that of PP (a), shows additional absorbance bands that can be attributed to the ester carbonyl group (1725 and 1180 cm^{-1}), and to the epoxy group [1256 cm^{-1} (shoulder), 900 and 845 cm]. Moreover, the absence of the absorption bands at 3140, 1640 cm^{-1} and 940, 815 cm^{-1}, unambiguously shows that graft polymerization occurred. These absorbance bands are specific to the unsaturated C=C group of the GMA monomer. The immobilization of β-CD onto PG is confirmed by the spectrum of PG-CD [Fig. 1(c)] that shows a significant decrease of the epoxy signals mentioned above and also by the appearance of large bands in the 2980–3680 cm^{-1} region and around 1100 cm^{-1}.

These results are supported by MAS and CP-MAS solid state NMR spectra, from which additional information about the filter structure can be deduced. The carbon-proton dipolar interaction in a cross polarization experiment (CPMAS) is very efficient for rigid structures, but becomes less effective when the mobility increases. If the sample is not homogeneous, the different phases can respond differently to the imposed conditions. The solid state high resolution NMR MAS techniques (with or without cross polarization), allow the rigid as well as the mobile phases to be highlighted.[14]

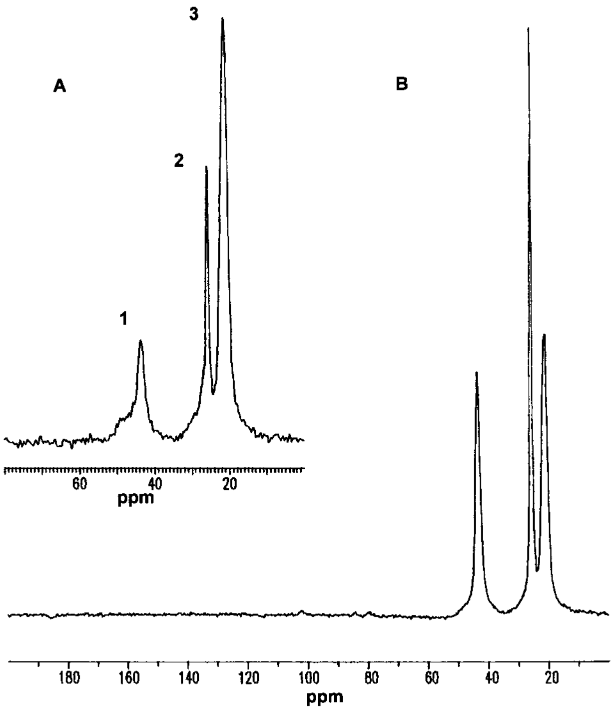


Figure 2 Solid state NMR spectra of PP: (A) MAS spectrum, and (B) CPMAS spectrum.

Figure 2 shows the MAS (A) and CPMAS (B) spectra obtained for the isotactic PP in the starting nonwoven fabric. The peak assignments (Table I) are in good agreement with the literature.[14,15] The two spectra show a different intensity for the methyl signal (C3); this signal increases in the MAS spectrum reflecting the

Table I Chemical Shifts of the Carbons of PP in Solid State ^{13}C CPMAS and MAS Experiments

	Carbon		
	1	2	3
CPMAS spectrum ppm	43.8	25.9	21.3
MAS spectrum ppm	43.4	25.6	20.9

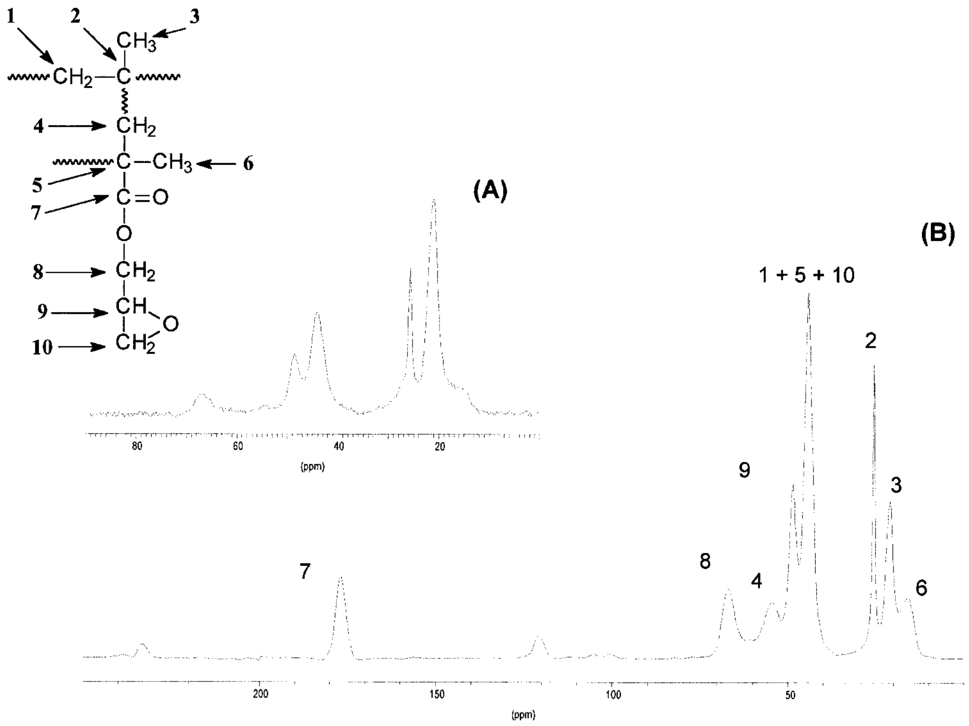


Figure 3 Solid state NMR MAS (A) and CPMAS (B) spectra of PG GMA = 408 wt % (NS = 21,032, 4.25 Khz).

greater mobility of this group. The shoulder between 40–50 ppm was observed only in the MAS spectrum and could be attributed to the presence of disordered structures as expected for a semicrystalline polymer.

Figure 3 represents the MAS (A) and CPMAS (B) spectra of PG support that consist of PP crosslinked with poly(glycidylmethacrylate) (polyGMA) grafted filter (GMA = 408 wt %). The signals of these spectra (Table II) were assigned from ^{13}C-NMR spectrum of polyGMA homopolymer and from the DEPT and high resolution ^{13}C spectra of GMA monomer in solution (data not shown). As expected, the signals caused by the double bond of the GMA monomer are not present in the spectrum whereas the epoxy signals can be clearly distinguished (labeled 9 and 10). The carbon of the carbonyl group of the ester (C7) appears at 176.9 ppm. It is worthwhile to note that the signals at 120 and 234 ppm are side bands resulting from the rotation of the carbonyl group. These signals can be found at a symmetrical distance from the C7 signal at 4250 Hz, which represents the rotation speed of the sample during the acquisition. There is also a new peak at 15.8 ppm that can be attributed to the CH_3 (C6) of the polyGMA chains. Paradoxically, the intensity of this signal does not increase in the MAS spectrum compared with the signal of the methyl group (C3) of PP (21.0 ppm). Analogously, the peaks attributed to C8 (67 ppm) and C4 (54.7 ppm) are less intense on the MAS spectrum than on the CP

Table II ^{13}C Assignment for Carbons in PG Support Measured by CPMAS and ^{13}C Spin Lattice Relaxation (T1) of the Carbons of PG Support by Torchia Sequence (GMA 80 wt %)

Chemical shift								
Carbon	7	8	4	9	1 + 5 + 10	2	3	6
ppm	176.9	66.9	54.7	48.6	44.4	25.6	21.0	15.8
T1 relaxation time (s)								
PP					37.7	21.9	0.63	
PG (GMA = 80 wt %)	11.1	1.4	7.1	1.8	10.0	21.7	0.6	

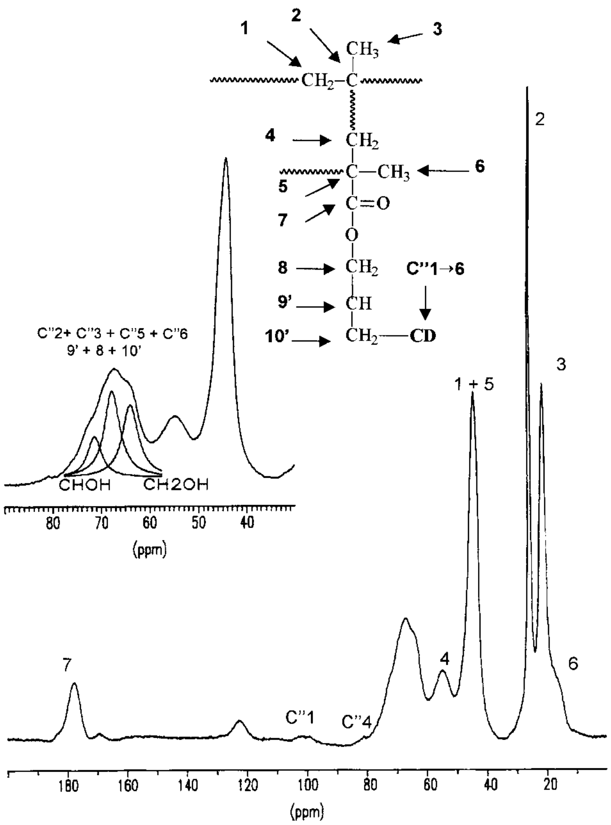


Figure 4 Solid state CPMAS NMR spectrum of PG-CD support β-CD = 130 μmol/g; GMA = 96 wt %.

MAS spectrum. On the other hand, the T1 values indicate a higher mobility of these signals with respect to those of PP. As shown in Scheme 1, the grafted polyGMA chain is probably linked to the PP polymer by the intermediate of an ether bonding.[7] In this case, the monomer units of both copolymers (PP and polyGMA) that are situated directly at the grafting sites should have different signals from the others. Although these sites are not statistically abundant, the corresponding modified signals were not detected.

As shown in Figure 4, the presence of β-CD is not easy to detect in the filters despite a grafting percentage of 15% in weight. The signal of the expected anomeric carbon does only weakly appear at 100 ppm. The presence of CD, however, is evident because of the broadened signal between 60 and 80 ppm compared with the one in the same region in Figure 3 relative to a PG support. This broad band may be the result of the overlapping of C″2, C″3, C″5, and C″6 signals of β-CD on one hand, and the signals of C8, C′9, and C′10 of the reacted epoxy groups of polyGMA on the other hand. This region usually corresponds to the CH_2OH and CHOH groups. C″1 and C″4 of β-CD can be observed at 105 and 85 ppm with more difficulty. The absence of the peak at 48.6 ppm previously present on the spectrum of PG in Figure 3 shows the transformation of the epoxy C10 upon reaction with β-CD. As a consequence, the former signal is shifted to the 60–80 ppm region on Figure 4.

The proton spin-lattice relaxation times (T1) and ^1H spin lattice relaxation in the rotating frame (T1ρ) have been measured to investigate the molecular mobility of the materials (Tables II and III) that consisted of PP, PG, and PG-CD supports. T1 values were obtained with the Torchia sequence.[16] The T1ρ values reflect the rate of the spin diffusion which is inversely related to the proton–proton intermolecular distance and to the intensity of molecular motions.

The molecular structure of filters with different GMA and β-CD add-on values has been analyzed in terms of relaxation parameters. As shown in Table III, the difference of magnitude of the values of T1ρ measured for the PP (C1: 43.8 ppm; C2: 25.9 ppm; C3: 21.3 ppm) and those of the

Table III Solid ^{13}C-NMR Chemical Shifts, ^{13}C Spin Lattice Relaxation (T1 in s) (Torchia Sequence) and ^1H Spin Lattice Relaxation in the Rotating Frame (T1ρ in ms) for Basic PP and PG-CD Supports

	PP			88% GMA 96 μmol β-CD/g			212% GMA 135 μmol β-CD/g			465% GMA 145 μmol β-CD/g		
Assignment	ppm	T1 (s)	T1ρ (ms)	ppm	T1 (s)	T1ρ (ms)	ppm	T1 (s)	T1ρ (ms)	ppm	T1 (s)	T1ρ (ms)
C8				64.4	6.9	3.5	64.3	5.7	4.4	64.4	6.3	4.2
C4				54.7	—	—	55.3	10.5	3.6	54.5	9.8	4.6
C1 (+C5)	43.8	37.7	20.5	44.1	33.2	18.7	44.2	25.3	15.6	44.9	9	5.5
C2	25.9	21.9	20.6	25.9	22.3	23.4	25.9	22.4	23.2	25.9	21.3	21.3
C3	21.3	0.6	19.4	21.2	0.6	21.1	21.3	0.6	21.6	21.3	0.6	16.1

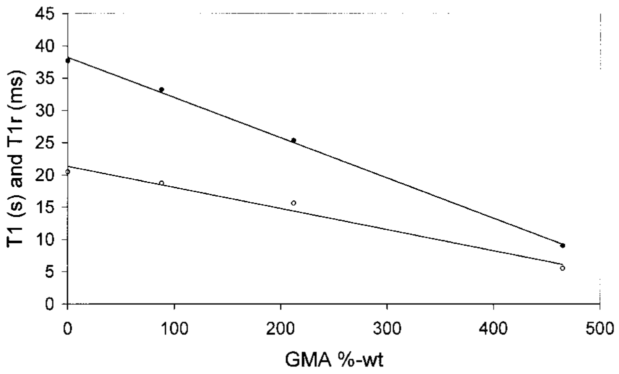


Figure 5 Variation of T1 (s) (filled symbols) and T1ρ (ms) (open symbols) of the CH_2 groups of the macromolecular chain of PP against GMA wt % on PG-CD samples.

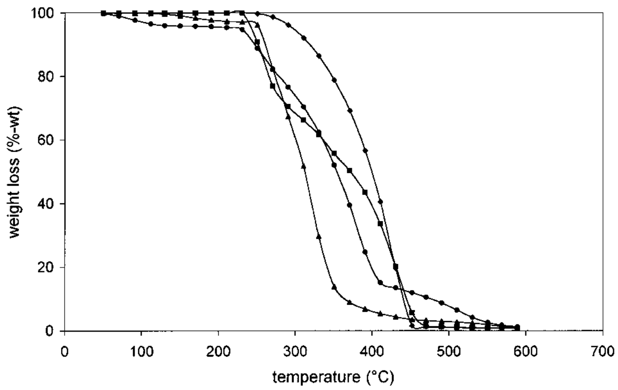


Figure 6 TGA thermogram of: ◆, PP; ▲, polyGMA; ■, PG GMA = 70 wt %; and ●, PG-CD grafted by 73 wt % GMA and 85 μmol/g of β-CD.

polyGMA reacted with β-CD (C8: 64.4 ppm and C4: 54.7 ppm) show clearly the presence of two phases with different dimensions: a small one (in the order of 1 nm) corresponding to polyGMA crosslinked with β-CD, and a larger one (in the order of 10 nm) corresponding to PP. Data given in Table III and Figure 5 exhibit a decrease of the values of T1 and T1ρ of the signal at 44 ppm. This signal corresponds to the superposition of C1 of the PP matrix and C5 of the polyGMA upon increase of the wt % GMA content in the PG-CD supports. For poorly grafted PP, the values of both relaxation parameters are close to those of pure PP, and they approach those of polyGMA as the grafting rate increases (see the values of T1 and T1ρ in Table II).

Furthermore, it is possible to observe a difference in the T1 values for the signals of the carbons at 64.4 and 54.7 ppm (corresponding to C8 and C4, respectively) that appear in Tables II and III, that are related to PG and PG-CD materials. The T1 values (Table II) relative to the carbons C8 and C4 of the grafted polyGMA on a PG sample indicate a superior mobility of the former (T1 = 1.3 s and 7.1 s on the average), compared with the corresponding groups in PG-CD. It can be noticed that the values of T1 for C8 and C4 are superior (T1 = 6.3 s and 10.1 s on the average) on the PG-CD filters. This indicates that the polyGMA chains probably undergo a reaction of their epoxy groups with several hydroxyl groups of one CD molecule, thus leading to a crosslinked polymer network. In addition, the rigidity of the samples may be enhanced by the appearance of a dense hydrogen bonding network between the hydroxyl groups of CD and those formed by the opening of the epoxide function upon the grafting reaction.

The TGA thermogram given in Figure 6 shows the different profiles of decomposition of the initial nonwoven PP and the intermediate PG. The temperatures corresponding to 2, 50, and 98% of weight loss of the measured samples were calculated (the dry weight at 200°C was taken as reference). The results are presented in Table IV and Figure 6. The half disappearance of polyGMA occurs at a temperature that is 85°C lower than that of PP and is consequently observed on the thermogram of the PG (GMA = 70 wt %) sample. The presence of β-CD can be detected from the different profile of the curve in the intermediate region and especially in the region above 400°C, that typically corresponds to the end of the decomposition of polyglycosidic compounds.

The calorimetric measurements have been realized using PP and PG samples with different compositions in polyGMA. The values for the

Table IV Values of the Temperatures (in °C) Corresponding to 2, 50, and 98% of Weight Loss under Thermal Decomposition of the Filters at Different Steps of Their Synthesis and of Their Separated Components

Sample	2% Weight Loss	50% Weight Loss	98% Weight Loss
PP	277	398	448
PG70	240	368	462
PG-CD	237	357	563
polyGMA	252	313	548
β-CD	315	348	564

Table V Values of Melting Temperature and the Corresponding Enthalpy Measured by DSC for PP Supports and PG Derivatives with Different GMA wt %

Sample	T_m (°C)	ΔH (J/g of Filter)
PP	167.0	89
PG20	167.2	84
	165.2	71
PG67	159.7	39
PG80	160.9	62
PG90	158.0	31
		36
		22
PG262	162.9	26
	154.8	13
PG352	155.7	24
	158.9	16
PG400	146.3	18

melting temperature (T_m) and the melting enthalpy (ΔH_m) are presented in Table V. The results obtained for PP indicate an isotacticity of 80%, and are in good agreement with the literature[17] and with what has been determined by solid NMR analysis. As shown in Table V, it was difficult to obtain reproducible calorimetric measurements. This is probably because of the heterogeneity of the aliquots of filter introduced into the measurement cell. As a result, only a slight decrease of the temperature of fusion was detected by increasing the percentage of grafted GMA. On the other hand, the melting enthalpy decreases with increasing rate of grafted GMA as displayed in Figures 7 and 8. In this study, the influence of the irradiation on the crystallinity of PP was not taken into account, but some authors have already reported that polyolefin irradiation might create both a change of their crystallinity and a decrease of ΔH_m.[18]

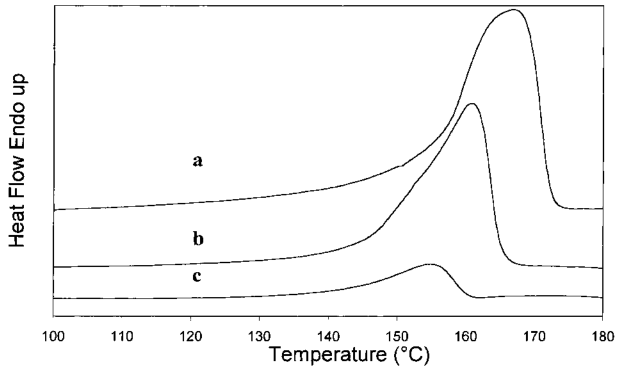


Figure 7 DSC diagrams of (a) PP; (b) PG, GMA = 80 wt %; and (c) PG, GMA = 352 wt %.

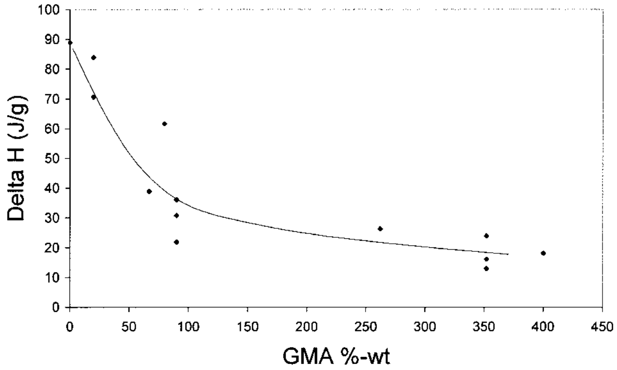


Figure 8 Variation of the melting enthalpy of the PG samples versus the GMA wt % measured by DSC.

PG samples with different rates of GMA have been observed by optical microscopy and the results are presented on Figures 9 and 10. In contrast with what is observed for the initial nonwoven PP, PG samples exhibit two kinds of fibers that differ in their diameters. The thin fibers have a diameter of 22–27 μm which corresponds to unreacted fibers or portions of fibers. The thick fibers are those that underwent the grafting of GMA. It was observed that the diameter varies with the measured GMA wt % of the sample. Figure 9 displays one end of a grafted fiber (GMA = 253 wt %) where the PP fiber protrudes as a core from the polyGMA sheath. Figures 9 and 10 confirm clearly that the GMA polymerizes by grafting onto the irradiated fibers rather than

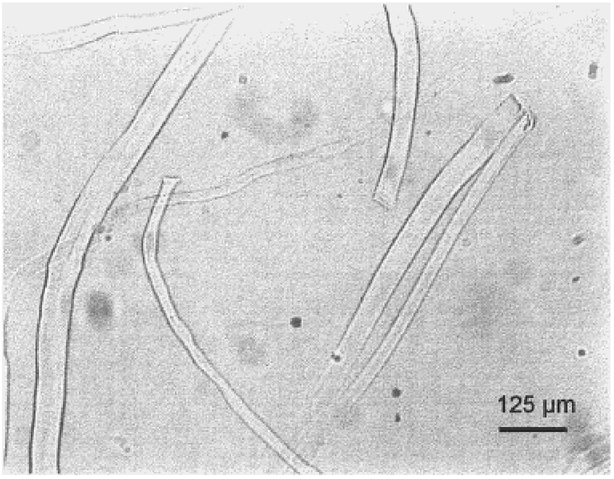


Figure 9 Mixture of grafted and nongrafted fibers in a PG sample with GMA = 144 wt % (×10).

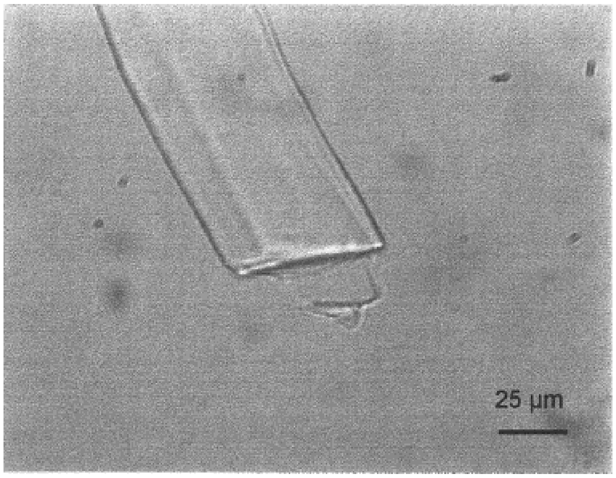


Figure 10 One end of a grafted fiber in PG sample with GMA = 253 wt % (×50).

randomly in the free volume of the nonwoven material. The presence of grafted and ungrafted fibers or portions of fibers on Figure 10 also confirms that the graft polymerization mainly concerns both irradiated surfaces of the fabric rather than the interior. Our electron beam equipment allows a uniform penetration of the electrons at a depth of approximately 100 μm into the material. The consequence is that the 2-mm-thick grafted nonwoven PP is submitted to a nonuniform exposure to the electron curtain. An improved homogeneity of the final material should be obtained by using a more energetic electron accelerator (1 MeV for example) that would provide a uniform penetration throughout the nonwoven fabric.

CONCLUSION

PP nonwoven fabric has been functionalized with the help of the original preirradiation grafting technique using electron beam activation. Different supports have been synthesized in two steps: graft polymerization of GMA onto filters followed by coupling with β-CD. The structure of these new materials was confirmed using FTIR, solid ^{13}C-NMR, TGA, and DSC techniques. These analytical investigations revealed the microstructure of the materials and its evolution under the different steps of the synthesis. On the other hand, optical microscopy has evidenced that, because of the relative low energy of our electron beam equipment, the grafting reaction occurred mainly only on both surfaces of the fabric, and let the bulk of the material unreacted. In the coming third part of this study, one of the possible applications of these CD functionalized materials will be presented—a description of how they are efficient in the removal of organic substrates from aqueous media will be described.

We gratefully acknowledge the financial support of the European Union through the FAIR programme, number CT 95 0300.

REFERENCES

1. Szejtli, J.; In Cyclodextrins and Their Inclusion Complexes; Akadenriai Kiado: Budapest, 1982, p. 162.
2. Okamura, K.; Kanuyama, S.; Murata, S.; Kubota, M.; Azuma, M. Jpn Kokai Tokkyo Koho 1994, JP 06, 116, 871.
3. Duchène, D. New Trends in Cyclodextrins and Derivatives. Edition de Santé; Paris, 1991.
4. Szente, L. J Therm Anal 1998, 51, 957.
5. Shao, Y.; Martel, B.; Morcellet, M.; Weltrowski, M. Can Text J 1996, 113, 145.
6. Shao, Y.; Martel, B.; Morcellet, M.; Weltrowski, M.; Crini, G. J Inclusion Phenom Mol Recognit Chem 1996, 25, 209.
7. Le Thuaut, P.; Martel, B.; Crini, G.; Maschke, U.; Coqueret, X.; Morcellet, M. J Appl Polym Sci, 2000, 77, 2118.
8. Denter, U.; Schollmeyer, E. J Inclusion Phenom Mol Recognit Chem 1996, 25, 197.
9. Poulakis, K.; Buschmann, H. J.; Schollmeyer, E. Pat. DE 40 35 378 A1, 1992.
10. Bushmann, H. J.; Denter, U.; Knittel, D.; Schollmeyer, E. J Text Inst 1998, 89, 554.
11. Reuscher, H.; Hirsenkorn, R.; Haas, W. Pat. EP 0 697 415 A1, 1995.
12. Reuscher, H.; Hirsenkorn, R. Pat. DE 19, 520, 967, 1995.
13. Crini, G.; Torri, G.; Leckchiri, Y.; Martel, B.; Janus, L.; Morcellet, M. Chromatographia 1995, 41, 424.
14. Bovey, F. A. In NMR Spectroscopy, 2nd ed.; Academic Press: New York, 1988; p. 399.
15. Bunn, A.; Cudby, M.E.A. J Chem Soc Chem Commun 1981, 15.
16. Torchia, D. A. J Magn Reson 1978, 30, 613.
17. Bandrup, J.; Immergut, E. H. Eds. Polymer Handbook, 3rd ed. John Wiley & Sons: New York, 1989.
18. Mukherjee, A. K.; Gupta, B. D.; Sharma, P. K. J Macromol Sci Macromol Chem Phys 1986, C26(3), 415.