

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

## I. Synthesis Parameters

PHILIPPE LE THUAUT,<sup>1</sup> BERNARD MARTEL,<sup>1</sup> GREGORIO CRINI,<sup>2</sup> ULRICH MASCHKE,<sup>1</sup>  
XAVIER COQUERET,<sup>1</sup> MICHEL MORCELLET<sup>1</sup>

<sup>1</sup> Laboratoire de Chimie Macromoléculaire, ESA 8009 CNRS, Université des Sciences et Technologies de Lille, 59655, Villeneuve d'Ascq Cedex, France

<sup>2</sup> Université de Franche Comté, Centre de spectrométrie, Route de Gray, La Bouloie 25030 Besançon, France

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**ABSTRACT:** A novel method for the preparation of immobilized  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrins ( $\alpha$ -,  $\beta$ -, or  $\gamma$ -CD) on polypropylene (PP) nonwoven fabrics is presented. These new materials were prepared by graft-polymerization of glycidyl methacrylate (GMA) onto PP filters using the electron-beam technique, followed by coupling of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs with the epoxide group. Optimization of various reaction parameters such as time, temperature, irradiation dose, monomer, and CD concentration was carried out. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2118–2125, 2000

**Key words:** cyclodextrin; filter; nonwoven; GMA, preirradiation; electron beam; polypropylene

## INTRODUCTION

Cyclodextrins (CDs), under their native, modified, or immobilized forms, are suitable for the decontamination of air streams or waste waters.<sup>1</sup> In our lab, we worked on the immobilization of CDs under the form of resins<sup>2</sup> or coated silicas,<sup>3</sup> which have shown good sorption capacities toward pollutants as pentachlorophenol, textile dyestuffs, and a wide variety of aromatic derivatives.<sup>4–6</sup> The aim of the present work was to immobilize CDs onto a nonwoven polypropylene (PP) support in order to obtain what is called “reactive filters.” Despite the fact that permanent grafting of CDs

onto fabrics was studied in the 1990s,<sup>7–9</sup> the obtained materials have never been developed for filtration technology. Furthermore, PP has, to our knowledge, never been used as a support among all the materials tested in the above-mentioned works, although PP has many advantages such as chemical and physical stability, a good resistance to biodegradation, and low cost. On the other hand, it is not possible to modify PP by using the conventional chemical methods. For that reason, a radiochemical method was applied, consisting of activation of the support by irradiation, followed by graft polymerization of a reactive monomer. Among the different radiochemical methods available (UV, plasma treatment,  $\gamma$ -irradiation, corona discharge), electron-beam irradiation<sup>10</sup> is convenient and effective, especially because of its moderate initiation reaction conditions (atmospheric pressure and temperature, air atmosphere). This technology can be applied to the following two methods: Grafting can be realized

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simultaneously or after the irradiation. The latter is called preirradiation and was applied in the present work. An additional advantage of the use of PP as a support in this type of process is that the hydroperoxide groups created under air irradiation have a stability that allows the grafting step to be done up to several months later.<sup>11,12</sup>

Irradiation-induced grafting is frequently used to modify polymeric materials and especially polyolefin films such as polyethylene (PE) and PP.<sup>13–15</sup> Many studies proved that the wettability,<sup>16</sup> adhesion,<sup>17</sup> dyeability,<sup>18</sup> and biocompatibility<sup>19</sup> properties of a given polymer can be changed by graft modification of its surface. It is thus possible, for example, to improve the water absorbency of a highly hydrophobic polymer by hydrophilization as well as to produce ion-exchange and ion-trap materials.<sup>20,21</sup>

Among the different monomers used for grafting, acrylic acid,<sup>22</sup> acrylamide,<sup>23</sup> and vinyl acetate<sup>24</sup> can be mentioned. In this work, we considered the glycidyl methacrylate (GMA) graft polymerization reaction to nonwoven PP. GMA is interesting because of the high reactivity of its epoxy groups. Indeed, the use of chemical reactions (amination, phosphorylation, sulfonation, hydrolysis)<sup>25–28</sup> leads to new materials that can be used for many other purposes, for example, metal chelation.<sup>27,29</sup> In this study, we adapted the method of Zhao et al. who linked  $\beta$ -CD onto polystyrene beads previously modified by GMA.<sup>30</sup>

In this article, we present the preparation of supports containing  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs. This new kind of material is obtained by a two-step process: The first step consists of irradiating the nonwoven PP in order to create hydroperoxide groups on its surface. This treatment is immediately followed by the graft polymerization of the GMA monomer initiated by the thermal degradation of the hydroperoxide groups. The result of this reaction we termed PG and consists of PP crosslinked with poly(glycidyl methacrylate) (polyGMA) chains. The second step involves the grafting of one of the CDs onto the nonwoven PG support by using its reactive epoxy groups, thereby yielding PG- $\alpha$ -CD, PG- $\beta$ -CD, or PG- $\gamma$ -CD filters.

A series of supports that differ in the nature and quantity of grafted CD and GMA was synthesized. The effect of different parameters such as irradiation dose, solvent composition, reaction time, and GMA or CD concentration are discussed in detail.

## EXPERIMENTAL

### Materials

The needled nonwoven PP fabric was 2 mm thick and had a surface weight of 100 g/m<sup>2</sup> (supplied by Texel Inc., Saint Elzéar De Beauce, Canada). Fibers were spun-bond and had a diameter of 25  $\mu$ m. Each sample had a 16-cm<sup>2</sup> area and was washed with acetone before treatment in order to remove lubricant from the fibers. The GMA monomer (Acros Organics, Geel, Belgium) was used without purification.  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs of analytical grade were supplied by Wacker GmbH (Munich, Germany). All other chemicals were of analytical reagent grade.

### Preirradiation

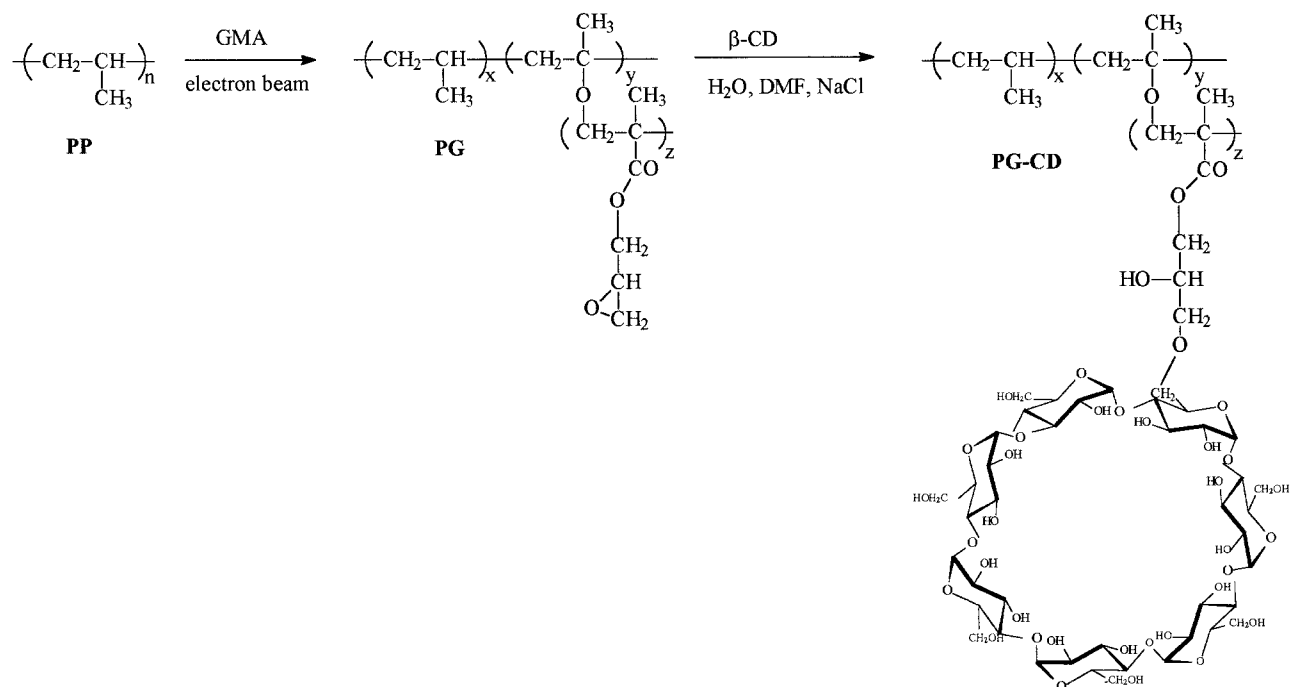
The electron-beam technique was employed to irradiate the PP samples. The generator used in our experiments was an Electrocurtain Model CB 150 (Energy Sciences Inc., Wilmington, DE), with an operating high voltage of 175 kV. The PP samples, prepared as mentioned above, were placed in a sample tray. This tray was passed under the electron curtain on a conveyor belt. The amount of energy required to irradiate products is called the dose. In our experiments, the unit dose applied by one pass was 50 kGy (5 Mrad). This was achieved by using a beam current of 2.4 mA and a conveyor speed of 0.15 m/s. The total dose range was between 50 and 250 kGy and was delivered in one to five repeated passes. All the irradiation experiments were carried out at room temperature in air. No temperature control during the irradiation process was applied. A time interval of 3 min elapsed between irradiation and dipping into the grafting bath.

### Reaction

See Scheme 1.

### Graft Polymerization Reaction

The technique introduced by Shkolnik and Behar<sup>31</sup> and developed by Harada et al.<sup>32</sup> was adapted. In a typical experiment, the monomer solution was prepared by mixing GMA in water-methanol (1:1, v/v), GMA representing 20% of the total volume (100 mL). Methanol was used to help the homogenization of the reaction bath while GMA is not miscible in water. Thirty minutes before immersion of the irradiated PP samples



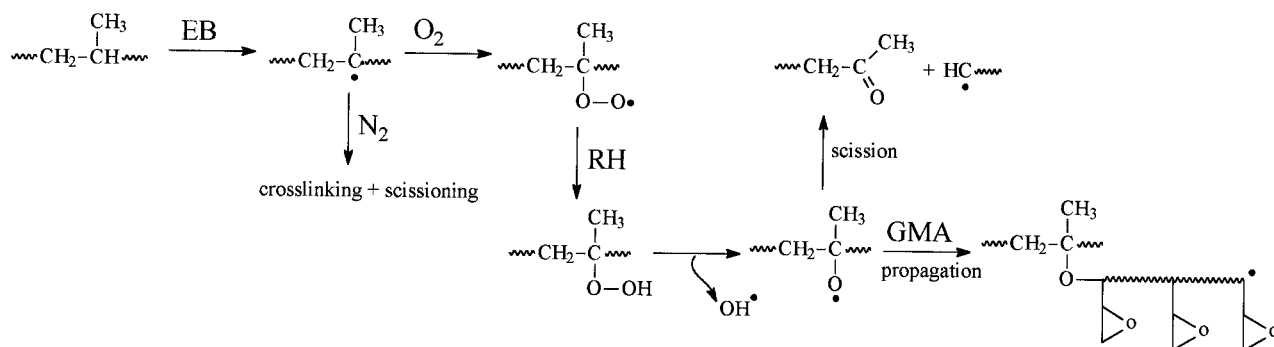
**Scheme 1** Summarized reaction path for the grafting of CD onto PP.

and during the whole reaction time, a constant flow of nitrogen gas was maintained in the vessel to remove traces of oxygen. The grafting reaction was conducted under magnetic stirring for the desired time. After the reaction, the sample was washed thoroughly for 12 h with acetone by a Soxhlet to remove all traces of the monomer and homopolymer absorbed onto the nonwoven PP material. It was then dried under a vacuum at 50°C and then weighed again. The weight percentage of the add-on of GMA (percent weight  $\times$  noted GMA %-wt) onto PP was calculated as percent weight GMA =  $100 \times (W_{PG} - W_{PP})/W_{PP}$ ,

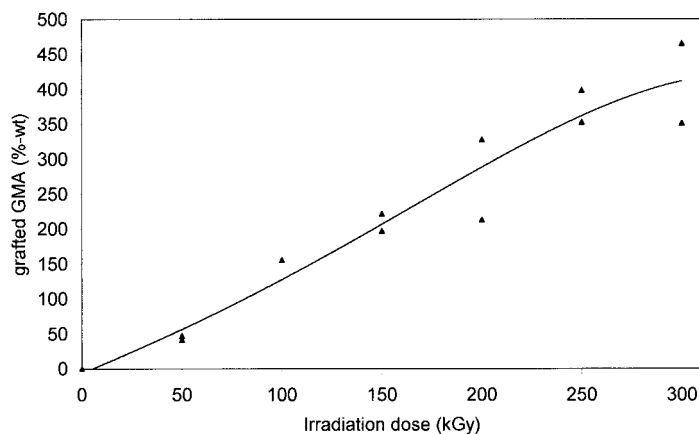
where  $W_{PP}$  and  $W_{PG}$  represent the weights of the initial PP and grafted PG sample, respectively.

#### Immobilization of CD onto PG

We adapted the method of Zhao et al. which consists of reacting CD with the epoxy groups in the presence of NaCl in a DMF-H<sub>2</sub>O mixture.<sup>30</sup> The PG sample was swollen in 100 mL of anhydrous dimethylformamide for 2 h. Then, 100 mL of an aqueous solution containing  $\alpha$ -,  $\beta$ -, or  $\gamma$ -CD and NaCl (1M) was added. The mixture was stirred at 80°C for the desired time. The final product was



**Scheme 2** Detailed phenomena occurring upon electron-beam irradiation of PP and mechanism for the initiation of the grafting reaction



**Figure 1** Influence of the preirradiation dose on the GMA weight percent-add-on to nonwoven PP; [GMA] = 20% vol in the reaction medium,  $T = 70^{\circ}\text{C}$ .

then washed with hot distilled water, dried, and weighed. The amount of grafted  $\beta$ -CD was determined from the weight gain of the support upon reaction and was expressed in micromoles of CD per gram of support and was calculated as follows:  $[(W_{\text{CD}} - W_{\text{PG}})/(W_{\text{CD}} \times M_{\text{CD}})] \times 10^6$ , where  $W_{\text{CD}}$  and  $W_{\text{PG}}$  represent the weights of the final CD grafted sample (PG-CD) and the initial PG sample, respectively.  $M_{\text{CD}}$  corresponds to the molar weight of the CD used. As the weight increase of the fabrics upon this step increased up to 20%, this value has been considered as sufficient and reliable for the CD determination.

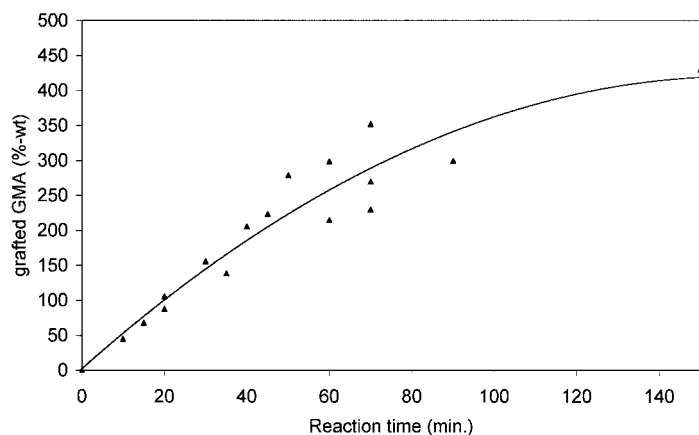
## RESULTS AND DISCUSSION

### Synthesis of PG Supports

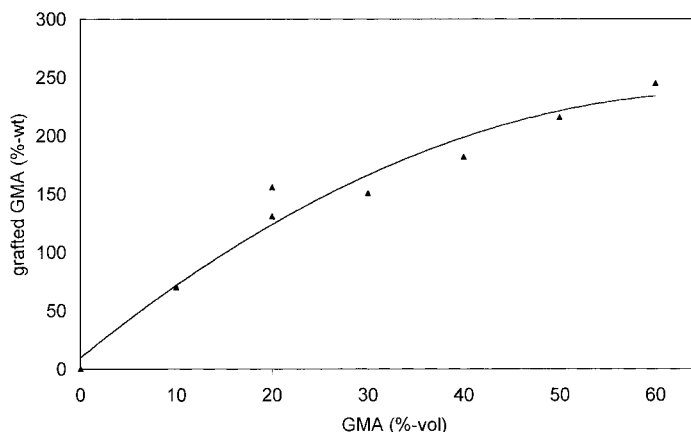
#### Irradiation of the Nonwoven PP

As described in the literature and summarized in Scheme 2, the irradiation of PP under nitrogen

leads to competition between scissioning and crosslinking, the latter being dominant when PP is irradiated in an inert atmosphere.<sup>33</sup> On the other hand, and according to our purpose, the irradiation under an air atmosphere is favorable to peroxide formation, which introduces some chemical instability by thermoxidation upon aging or during chemical functionalization, but also allows the desired initiation of the graft polymerization. As reported in Figure 1, the grafting rate of GMA increases continuously with the dose for a reaction time of 30 min at  $70^{\circ}\text{C}$ . Although doses superior to 250 kGy resulted in the visible disintegration of the PP support, which is attributable to an important polymer chain scission phenomenon. We experimentally observed the absence of any gel fraction by xylene extraction, confirming that crosslinking of the PP material was a minor process upon the applied dose range. The fiber degradation is probably due to the PP chain scis-



**Figure 2** Influence of reaction time on the GMA percent weight add-on to nonwoven PP; [GMA] = 20 % vol in the reaction medium;  $T = 70^{\circ}\text{C}$ .



**Figure 3** Influence of the volume ratio of GMA in the grafting bath on the GMA percent weight add-on to the nonwoven PP; other components of the reaction mixture: MeOH/H<sub>2</sub>O = 1 : 1; reaction time = 30 min; irradiation dose = 100 kGy;  $T = 70^{\circ}\text{C}$ .

sioning as classically reported in the thermooxidation phenomena of PP<sup>34</sup> as proposed in Scheme 2. These results also confirm the difference of behavior between PP and PE upon electron-beam irradiation under an air atmosphere; contrary to PE, PP undergoes more scissioning. In another study, Harada et al.<sup>32</sup> observed that the grafting reaction of acrylic acid onto PE (under nitrogen) decreased for doses superior to 20 kGy because of the occurrence of the crosslinking phenomenon that is unfavorable to the diffusion of the monomer into the polymer matrix.

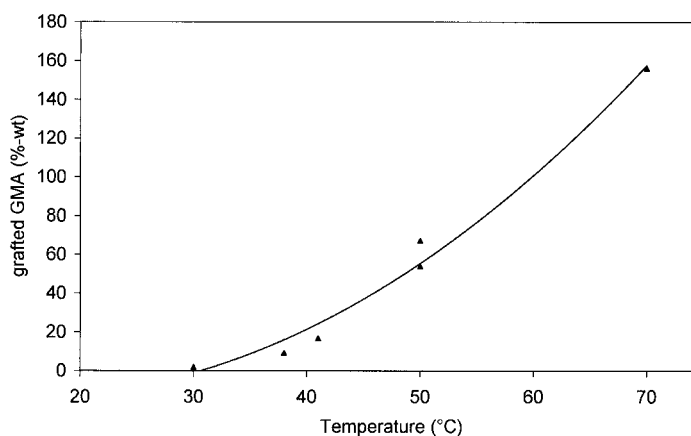
#### **Influence of Reaction Time**

The effect of the reaction time in the range of 10–150 min on GMA %-wt onto PP is represented

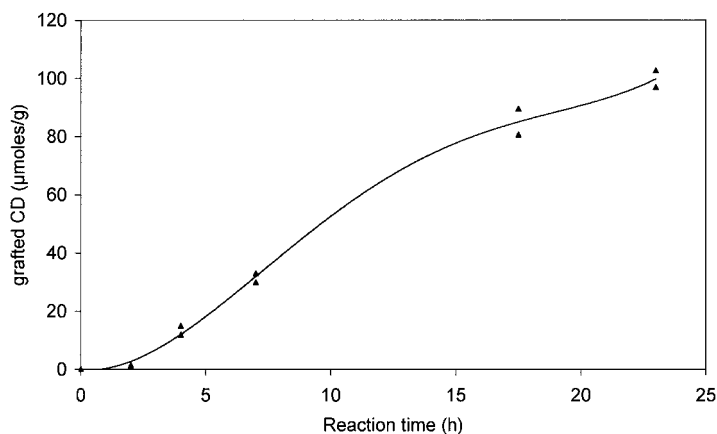
in Figure 2. The percentage of GMA grafting increased continuously with increasing reaction time. The percentage of grafting reached 100% wt after 20 min. For reaction times longer than 2 h, the GMA %-wt approached an asymptotic value of about 400% wt. Nevertheless, it has been observed that for GMA add-on values superior to 200% wt the rigidity and the brittleness of the resulting material would prevent its use as a filter.

#### **Influence of Monomer Concentration**

Figure 3 shows the GMA %-wt as a function of the volume ratio of the monomer in the reaction bath for a 30-min reaction time at 70°C. An optimum value was reached for 60% of GMA [40% of



**Figure 4** Dependence of the GMA percent weight add-on to the nonwoven PP upon the temperature; reaction time = 30 min. [GMA] = 20% vol in the reaction medium; Irradiation dose = 100 kGy.



**Figure 5** Influence of reaction time on the grafting rate of  $\beta$ -CD onto PG support; GMA % wt = 75%; [NaCl] = 0.5 mol/L; DMF/H<sub>2</sub>O vol ratio = 1 : 1;  $T$  = 80°C; irradiation dose = 100 kGy.

MeOH—H<sub>2</sub>O (1–1) mixture]. An increase of the viscosity of the reaction medium observed by capillary viscosity was an indication for the occurrence of a homopolymerization side reaction, proportional to the initial GMA concentration in the reaction medium. Considering our purpose of using the materials as filters, the GMA %-wt of 100–200% was established as the targeted addition. So, the corresponding volumic ratio of GMA levels to 20%.

#### *Influence of Temperature*

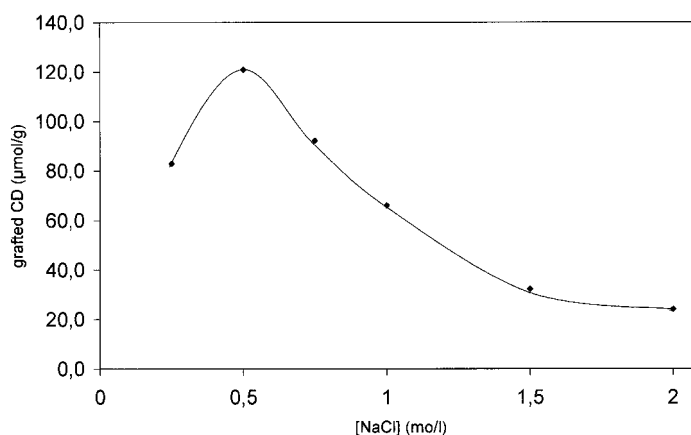
The relationship between graft percentage and reaction temperature is demonstrated in Figure 4. The degree of grafting increased regularly when the temperature applied was over 30°C. This is in agreement with the strongly positive

values of the activation energy of the decomposition of the hydroperoxide groups.<sup>35</sup> It was observed that the reaction medium was monophasic above 55°C; on the other hand, temperatures superior to 75°C led to methanol loss by evaporation and thereby to difficulties in the control of the reaction. Therefore, 70°C was chosen as the optimal temperature.

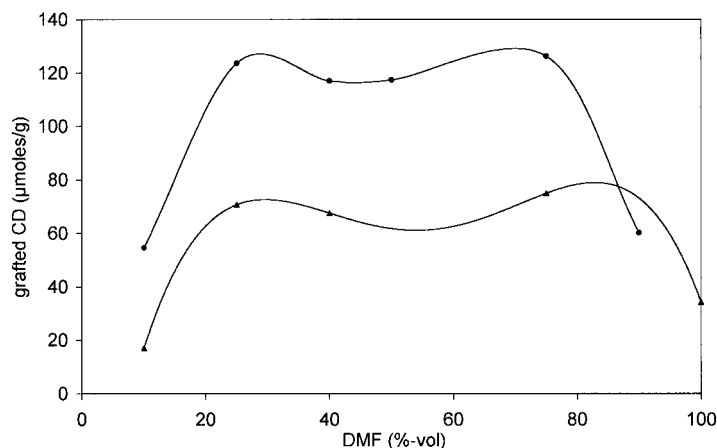
#### **Synthesis of PGCD Supports**

##### *Influence of the Reaction Time*

As shown in Figure 5, the maximum yield of the grafting reaction of  $\beta$ -CD onto the PG support (GMA = 75% wt) is attained within 24 h. This represents a grafting yield of 3.5% in weight with regard to the  $\beta$ -CD initially introduced into the reaction bath.



**Figure 6** Influence of the NaCl concentration on the grafting rate of  $\beta$ -CD; GMA % wt = 106%; DMF/H<sub>2</sub>O vol ratio = 1 : 1;  $T$  = 80°C; reaction time = 24 h.



**Figure 7** Influence of the DMF volume ratio in the reaction medium for the grafting of  $\beta$ -CD onto PG supports with two different GMA wt %-wt = (▲) 65% and (●) 384%; reaction time = 24 h.

#### *Influence of the NaCl Concentration*

As represented in Figure 6, the sodium chloride concentration has a prominent influence on the opening of the epoxide groups by the  $\beta$ -CD. It has been observed that the maximum yield occurred in the presence of 0.5 mol per liter of NaCl. These reaction conditions are rather milder than those applied in the polymerization of CDs by diepoxy compounds or by epichlorohydrin that generally require NaOH as a catalyst with a 10–30% range weight concentration.

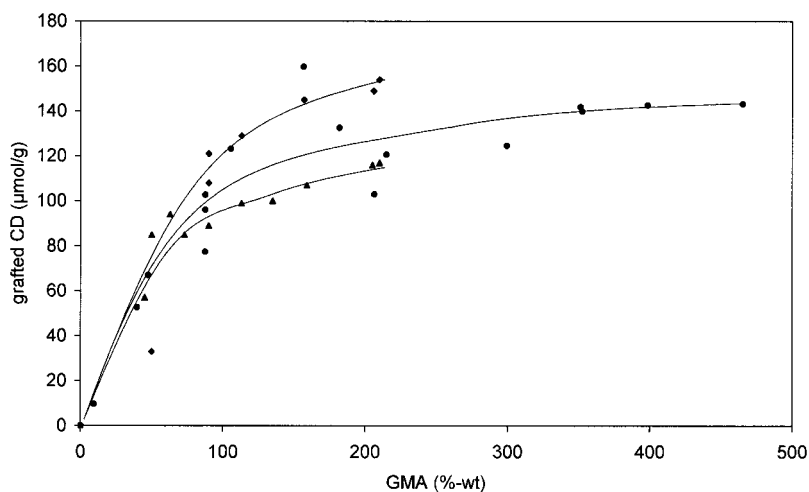
#### *Influence of the Solvent Composition*

The DMF–H<sub>2</sub>O ratio was adjusted by adding different volumes of the NaCl– $\beta$ -CD–H<sub>2</sub>O solution

to the constant volume of DMF containing the swollen PG samples. The optimal volume ratio of DMF in the reaction medium (DMF/H<sub>2</sub>O) ranges between 20 and 80% for two samples whose initial GMA percent weight was 65% wt and 384% wt (Fig. 7). DMF improved the wettability of the PG support that was strongly hydrophobic and, thereby, improved the reaction yield.

#### *Influence of the Weight Percent GMA on PG Supports*

The amount of fixed  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD is dependent upon the GMA %-wt on the nonwoven PG fabric as reported in Figure 8. In all cases, a plateau was reached for a GMA add-on superior to about 200%



**Figure 8** Influence of the GMA percent weight on the PG supports on the grafting rate of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs. [NaCl] = 0.5 mol/L, DMF/H<sub>2</sub>O vol ratio = 1–1;  $T$  = 80°C; reaction time = 24 h; CD/GMA mol ratio = 1 : 1; (◆)  $\alpha$ -CD; (▲)  $\beta$ -CD; (■)  $\gamma$ -CD.

(or 2.5 mmol/g of support). In the increasing portion of the curves, the molar ratio of epoxide groups/grafted CD is, on average, equal to 35. This means that fixed  $\beta$ -CD represents 3% (in mol) of the epoxy groups present on the PG support. Nevertheless, more than one OH group of CD may be involved in the reaction, so the fraction of reacted epoxy groups is probably over 3%. The results reported in Figure 8 also show that the grafting of  $\alpha$ -CD is superior to that of the other CDs tested.

## CONCLUSIONS

This work consisted of the grafting of CDs onto a PP material and optimizing the parameters of reaction. We proposed here a procedure that permits one to control both the GMA and CD content of the filters. In the following studies, additionally to the physicochemical characterization of the products, we will report the influence of the amount of CD and GMA grafted onto the PP fibers on the sorption capacities of the PG-CD filters.

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