

# Hydrogen Peroxide Initiated Grafting of Acrylamide onto Poly(ethylene terephthalate) Fibers in Benzyl Alcohol

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## SYNOPSIS

The grafting of acrylamide onto poly(ethylene terephthalate) fibers using hydrogen peroxide as the redox initiator was investigated. Benzyl alcohol was found to be the favorite medium for this grafting. Maximum graft yield (7.6%) was reached at 95°C; the graft yield decreased at higher temperatures, and finally grafting was inhibited at 120°C. The effect of monomer and initiator concentration on grafting was also studied. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The grafting of vinyl monomers onto natural and synthetic polymers have been reported by various workers recently.<sup>1-4</sup> Poly(ethylene terephthalate) (PET), in fiber form, is one of the polymers that was attempted to be modified by graft copolymerization. Many vinyl monomers such as acrylic acid,<sup>5,6</sup> methacrylic acid,<sup>7</sup> and methyl methacrylate<sup>8,9</sup> were used for grafting onto PET fibers.

The grafting studies onto PET fibers revealed that polymerization medium and the initiator used have important effects on grafting. For instance, it was reported that the grafting medium of 80% DMF(aq) increased the graft yield of glycidyl methacrylate onto PET fibers using benzoyl peroxide,<sup>10</sup> while the same grafting medium decreased the graft yield of the same monomer onto PET fibers using hydrogen peroxide as an initiator.<sup>11</sup> Similarly, the solvents added to polymerization medium can effect the grafting in a positive or negative way, and sometimes it can be totally inhibited.<sup>5,7,11</sup>

There are only a few studies concerning the grafting of acrylamide onto PET fibers.<sup>12,13</sup> We have also reported the grafting of acrylamide onto PET fibers using benzoyl peroxide recently.<sup>14</sup> There are no studies in the literature concerning the grafting of acrylamide onto PET fibers using hydrogen peroxide as an initiator. This article reports the grafting

of acrylamide onto PET fibers using hydrogen peroxide in benzyl alcohol medium.

## EXPERIMENTAL

### Materials

The experiments were carried out using multifilament PET fibers (30 filament, 110 dTex) obtained from SASA Co. (Adana). The PET fiber samples in small hanks were Soxhlet-extracted with acetone for 8 h. Hydrogen peroxide (Merck), benzyl alcohol (Merck), and acrylamide were chemically pure grade.

### Procedures

The graft copolymerization method was previously described in detail.<sup>14</sup> The fiber sample was placed into the polymerization tube containing required amount of monomer and initiator. The total volume was made up to 20 mL using distilled water, benzyl alcohol, or benzyl alcohol/water mixture, depending upon the experimental conditions. The mixture was purged with nitrogen for 20 min and the polymerization tube was placed into a water bath (Lauda D 40 S, Germany) where temperature could be controlled to within  $\pm 0.1^\circ\text{C}$ . The nitrogen purging was continued throughout the grafting reaction, which also facilitated the mixing of the polymerization system. The fiber sample taken from the polymerization medium at the end of the predetermined po-

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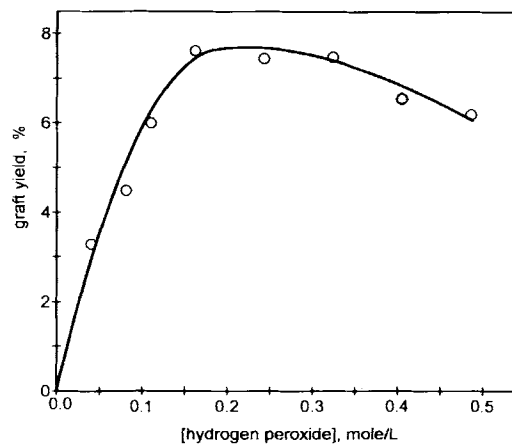
lymerization period was washed with boiling water several times then Soxhlet-extracted with water for additional 8 h. Finally, the fiber sample was dried and weighed, and the graft yield was gravimetrically determined from the weights of grafted and original fibers.

The FTIR spectra were recorded by using a Mattson 1000 Model spectrophotometer.

## RESULTS AND DISCUSSION

The first attempts of grafting PET fiber with acrylamide using hydrogen peroxide was carried out in aqueous media. This grafting experiment were performed up to 4 h, changing the monomer and initiator concentrations and the temperature between 0.35–4.22 mol/L, 0.04–0.49 mol/L, and 60–95°C, respectively. It was observed that there were practically no grafting in aqueous media.

It was reported that the use of preswollen PET fibers<sup>15,16</sup> in grafting or the addition of swelling agents to the graft copolymerization media<sup>10</sup> have positive effects upon the graft yield. In this study, we chose benzyl alcohol as the swelling agent. The experiments were reperformed using preswollen fibers or nonswollen fibers in benzyl alcohol/water mixtures. Table I shows that performing the polymerization in a medium containing benzyl alcohol gives satisfactory result. The increase in benzyl al-



**Figure 1** Variation of graft yield with hydrogen peroxide concentration; time 4 h; temperature 95°C; [acrylamide] 1.83 mol/L.

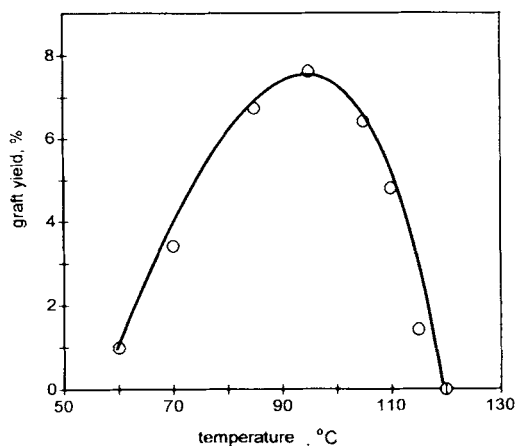
cohol/water ratio caused an increase in graft yield. The highest graft yield was obtained in pure benzyl alcohol (7.6%). Thus, all the following experiments were carried out in this medium.

The reproducibility of experimental results was checked by repeating some grafting experiments several times. It was observed that the deviation of graft yields was  $\pm 0.3$ . These deviations may be attributed to occluded homopolyacrylamide into the grafted PET fiber, although it has been extracted with water many times.

**Table I** The Effect of Benzyl Alcohol on the Grafting of Acrylamide onto PET Fibers Using Hydrogen Peroxide

Procedure	Graft Yield, %
a) PET fibers were kept in benzyl alcohol for 24 h at room temperature, blotted between filter papers, and then subjected to graft copolymerization in aqueous media. <sup>a</sup>	0.0
b) PET fibers were kept in 10 mL benzyl alcohol containing 2 g monomer for 24 h at room temperature, blotted between filter papers, and then subjected to graft copolymerization in aqueous media. <sup>a</sup>	0.5
c) PET fiber were subjected to the preswelling process of 100°C (above glass transition temperature of PET) for 5–40 min, blotted between filter papers, and then subjected to graft copolymerization in aqueous media. <sup>a</sup>	0.0
d) PET fibers were subjected to graft copolymerization in media having various benzyl alcohol/water (v/v) ratios as follow: <sup>a</sup>	
Benzyl alcohol/water (v/v)	
00/100	0.0
30/70	2.3
50/50	4.1
70/30	5.9
100/00	7.6

<sup>a</sup> Graft copolymerization conditions: temperature 95°C; time 4 h; [acrylamide] 1.83 mol/L; [hydrogen peroxide] 0.16 mol/L.



**Figure 2** Variation of graft yield with temperature; time 4 h; [acrylamide] 1.83 mol/L; [hydrogen peroxide] 0.16 mol/L.

The effect of initiator concentration upon the graft yield was investigated by changing the hydrogen peroxide concentration between 0.04–0.49 mol/L, and the results were shown in Figure 1. The graft yield increases with the initiator concentration at the beginning, reaches a maximum at 0.16 mol/L, and slowly decreases thereafter.

This type of relation between graft yield and initiator concentration is frequently observed in chemical grafting studies onto PET fibers.<sup>5,11,14,15</sup> The increase in the initiator concentration increases the concentration of hydroxyl radicals, which promote the grafting. Hydroxyl radicals also initiate homopolymerization of acrylamide in the bulk of the solution. These active homopolyacrylamide chains may give chain reaction with PET macromolecules and form sites suitable for grafting. However, the increase of the concentration of radicalic species with the increase in the initiator concentration above 0.16 mol/L promotes the termination reactions and causes a decrease in graft yield, as shown in Figure 1.

Because many of the chemical grafting studies are carried out in aqueous media,<sup>5-9,11-15</sup> the highest temperature attainable is limited with the boiling temperature of water. However, when the grafting is performed in benzyl alcohol, which has a boiling temperature of 205°C, it is possible to carry out the grafting at a higher temperature than in water.

Figure 2 shows the graft yields obtained between 60–120°C. The graft yield increases with the increase in temperature up to 95°C then shows a rapid decrease and goes to a very low value of 1.5% at 115°C. At 120°C there was practically no grafting. Figure

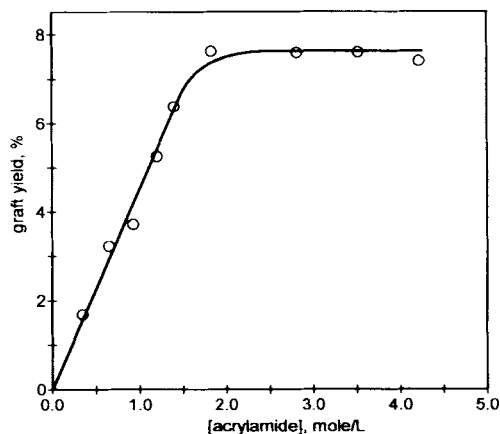
2 signifies that graft yield decreases and can even stop at sufficiently high temperatures.

The increase in temperature has an important effect on the swellability of PET fibers as well as its promotive effect on the decomposition rate of initiator and the rate of initiation and propagation.

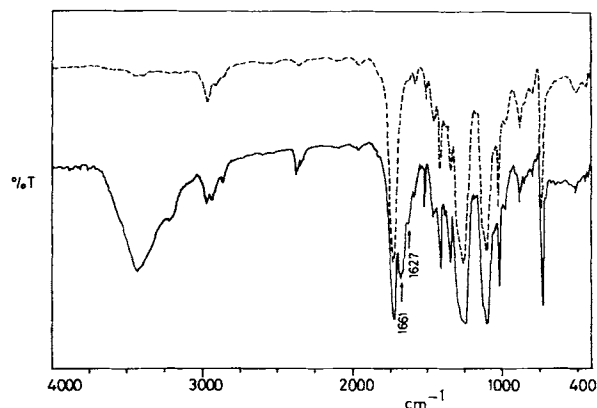
The increase in temperature especially around glass transition temperature causes polymer going from a glassy state to a highly viscous state, increasing the mobility of the polymer chains and, thus, increasing their tendency to give radicalic reactions.<sup>17</sup> However, any further increase in temperature causes a similar effect as in the increase in initiator concentration and promotes the termination reactions. In addition, the increase in diffusion rate also activates the termination reactions. As a result of the termination reactions, the graft yield decreases above certain temperature (95°C for our system).<sup>14,17</sup>

When the effect of monomer concentration upon graft yield was investigated, it was seen that the graft yield increased up to the monomer concentration of 1.83 mol/L, and remained constant around 7.6% above this value (Fig. 3).

Obviously, the increase in the monomer concentration increases the number of acrylamide molecules in the bulk of the solution, which can diffuse into the PET fibers. This increases the probability of PET macroradicals and growing grafted side chains to find monomer units to add and, therefore, increases the graft yield. All these are valid up to a acrylamide concentration of 1.83 mol/L. The fact that graft yield does not increase above this concentration can be attributed to the factors such as physical adsorption of monomer and the deposition



**Figure 3** Variation of graft yield with acrylamide concentration; time 4 h; temperature 95°C; [hydrogen peroxide] 0.16 mol/L.



**Figure 4** FTIR spectra of ungrafted (----) and 7.6% acrylamide grafted (—) PET fibers.

of acrylamide homopolymer onto PET fibers and the behavior of grafted side chains as a barrier inhibiting the diffusion of the reactants into the fibers.<sup>5,6</sup>

Figure 4 shows the FTIR spectra of ungrafted and 7.6% acrylamide grafted PET fibers. The grafted fibers spectrum exhibits NH stretching bands at 3200–3450  $\text{cm}^{-1}$ , CO amide peaks at 1661  $\text{cm}^{-1}$ , and CN resonance peak at 1627  $\text{cm}^{-1}$ , coming from the grafted polyacrylamide.

In conclusion, this study proved that acrylamide can be grafted onto the PET fibers in benzyl alcohol medium using a water-soluble initiator such as hydrogen peroxide. The use of benzyl alcohol as grafting medium provides the examination of the effects of high temperatures on grafting. The optimum conditions for the maximum grafting (7.6%) were found to be 95°C, 1.83 mol/L monomer concentration, and 0.16 mol/L initiator concentration.

We are grateful to Ankara University Research Fund for their financial support of this work (Project Number: 93-25-00-34).

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Received February 23, 1995

Accepted September 1, 1995