

H₂O₂-Induced Graft Polymerization of Acrylic Acid on Poly(ethylene Terephthalate) Fibers

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Synopsis

Graft polymerization of acrylic acid to poly(ethylene terephthalate) fibers using H₂O₂ as initiator was only possible in benzyl alcohol as reaction medium. The effect of initiator and monomer concentrations, reaction time, and temperature as well as addition of metallic salts to the polymerization medium was studied. Percent grafting was enhanced significantly by increasing H₂O₂ concentrations up to 100 mequiv/L and then decreased upon further increase in initiator concentration. The same held true for acrylic acid concentration of up to 10%, but above this concentration grafting leveled off. Raising the polymerization temperature from 85 to 115°C favored grafting at lower H₂O₂ concentration. The reverse was the case at higher H₂O₂ concentration (more than 25 mequiv/L). Addition of copper sulfate to the polymerization medium decreased the rate of grafting, and no leveling off of grafting could be achieved even after 5 h. The ferrous ammonium sulfate functioned similarly but to lesser degree, and leveling off of grafting occurred after 4 h. This contrasted with grafting in the absence of metallic salts where grafting leveled off after 1 h. Action of initial graft formation as diffusion barrier is believed to account for this.

INTRODUCTION

Chemical modification of poly(ethylene terephthalate) fibers (PET) by graft polymerization has been studied by many authors, and the subject has recently been reviewed by us.¹ Vinyl graft polymerization onto PET could be initiated by high-energy radiation using γ -rays from Co 60,²⁻¹¹ x-rays, or high-energy electrons from accelerators,^{7,13-15} or by chemical means using different initiators such as benzoyl peroxide,^{12,16,17} hydrogen peroxide,^{18,19} persulfate,^{18,20} ceric ions,²¹ azobisisobutyronitrile,^{18,22} or oxygen at high temperatures.²³⁻²⁷ Of the vinyl monomers used for such grafting were styrene,^{2,3,16,18,22,23} 4-vinylpyridine,^{4,28} acrylonitrile,^{5,6,20,29} acrylic and methacrylic acid,^{11,14,17,21,27,30-38} vinyl acetate,¹⁵ *N*-vinyl-3-morpholinone,³⁹ and 2-methyl-5-vinylpyridine.^{12,19,40}

In the present paper, grafting of acrylic acid to PET fibers in a swelling solvent (benzyl alcohol) using H₂O₂ as initiator is reported.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) fibers (PET-Tergal, Hoechst, 1.2 den/40 mm, cotton type) were purified via a mild cleaning treatment with sulfonated fatty alcohol (2 g/L) for 30 min at 65°C, rinsed with hot and cold water, dried at room temperature, and finally Soxhlet extracted with methanol for 24 h to remove any material adhering to the surface. Acrylic acid was freed from the inhibitor by vacuum distillation before use.

Hydrogen peroxide (Merk), copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), and ferrous ammonium sulfate [$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$] were analytical-grade chemicals. Benzyl alcohol (BDH) was laboratory grade.

Graft Polymerization Procedure

Unless otherwise indicated, the graft polymerization reaction was carried out as follows: In a 50-mL stoppered conical flask, PET fiber (0.5 g) was introduced into 50 mL benzyl alcohol containing the monomer. The flask was immediately stoppered and placed in a thermostated water bath for a certain period until the required temperature was reached, and the initiator was then added. The contents were stirred occasionally during polymerization. After the desired reaction time, the contents were filtered on a sintered glass crucible, and the sample was immediately washed to stop the reaction and to remove homopolymer formed during the process. Since the polymer (polyacrylic acid) is water soluble, washing was done with plenty of water, boiling the sample several times in water, and finally drying under reduced pressure till constant weight was obtained.

To ensure complete removal of homopolymer, the sample was dissolved in a mixture of phenol-tetrachloroethane (85:15) using a material-to-liquor ratio of 1:200 and precipitated by addition of excess amount of methyl alcohol. The precipitate was then washed several times with boiling water and again boiled in water for 3 h, then filtered and dried at 105°C for 4 h, followed by cooling over P_2O_5 .

Percent grafting was calculated from the difference in the dry weight of the sample before and after the treatment, thus:

% grafting =

$$\frac{(\text{dry weight of grafted sample}) - (\text{dry weight of original sample})}{\text{dry weight of original sample}} \times 100$$

RESULTS AND DISCUSSION

Preliminary experiments of grafting acrylic acid (AA) to PET fibers in aqueous medium resulted in very little or practically no grafting. This necessitated the use of nonaqueous medium. In the present study, benzyl alcohol was used as a medium for grafting AA to PET fibers. As can be seen in Table I, substantial grafting occurred upon using benzyl alcohol as a medium.

Hence, in order to discover the optimal condition for grafting AA to PET fibers, the polymerization reaction was carried out in the swelling solvent (benzyl alcohol) at different temperatures for varying lengths of time using different concentrations of initiator and monomer. The effect of addition of metallic salts to the polymerization medium on percent grafting was also investigated.

Initiator Concentration

The effect of H_2O_2 concentration on percent grafting was studied at different initiator concentrations. The latter ranges from 10 to 1000 mequiv/L H_2O_2 . The results obtained are shown in Figure 1. It is seen that increasing the H_2O_2 concentration up to 100 mequiv/L is accompanied by a significant enhancement

TABLE I

Polymerization conditions	Graft yield, %
(1) PET fibers (0.5 g) were treated with ferrous ammonium sulfate solution (0.1%) for 1 hr, blotted between filter papers, and then introduced in a solution containing AA (10%) and H ₂ O ₂ (30 mequiv/L) at 85°C for 4 h at a material-to-liquor ratio of 1:100.	1.2
(2) PET fibers (0.5 g) were swollen in benzyl alcohol for 1 h at room temperature (ca. 30°C), blotted between filter papers, and then introduced in the polymerization solution as above.	1.4
(3) PET fibers (0.5 g) were swollen in benzyl alcohol at 90°C for 30 min, blotted between filter papers, immersed in ferrous ammonium sulfate (0.1%) for 1 h at room temperature (ca. 30°C), blotted again between filter papers, and then introduced in the polymerization solution as indicated above.	0.6
(4) PET fibers (0.5 g) were immersed in benzyl alcohol containing AA (10%) and H ₂ O ₂ (30 mequiv/L) at 85°C using a material-to-liquor ratio of 1:100 for 4 h.	3.8

in percent grafting. Further increase in H₂O₂ concentration decreases grafting substantially. A similar trend was reported for grafting 2-methyl-5-vinylpyridine to PET fibers.¹⁹ This suggests that PET and H₂O₂ form a redox system which decomposes to yield hydroxyl radicals. These hydroxyl radicals attack the PET molecules to produce PET macroradicals capable of initiating grafting. The hydroxyl radicals also attack the monomer to yield ultimately homopolymer. Initiation of grafting can also occur via chain transfer; growing homopolymer chains may be terminated by PET molecules to give rise to PET macroradicals. At higher H₂O₂ concentration, abundance of hydroxyl radicals is expected. As a result, participation of the hydroxyl radicals in termination process with growing polymer chains and PET macroradicals as well as self-reaction (combination) would be favored over graft initiation, thereby decreasing grafting.

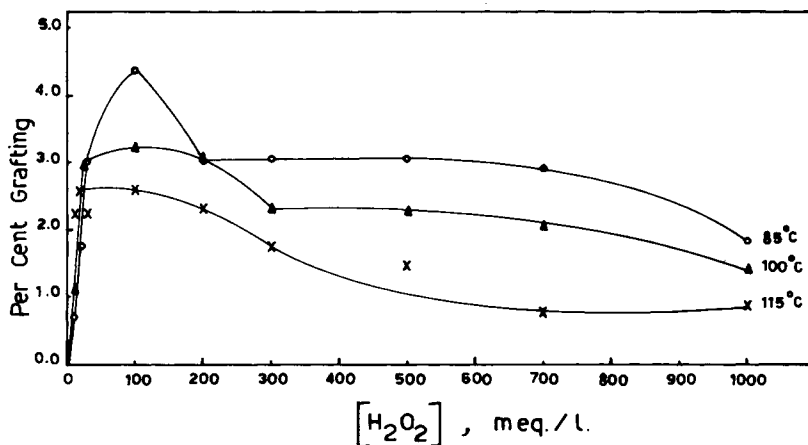


Fig. 1. Influence of hydrogen peroxide concentration on graft yield at different temperatures: (●) 85°C; (▲) 100°C; (x) 115°C; [AA], 10%; reaction time, 4 h; material:liquor ratio, 1:100.

Polymerization Temperature

Figure 1 shows the effect of polymerization temperature on grafting AA to PET fibers using H_2O_2 as initiator. The effect is found to be related to initiator concentration. A pronounced acceleration effect is observed during grafting using lower initiator concentrations (not more than 25 mequiv/L H_2O_2). The opposite holds true for higher H_2O_2 concentrations since raising the polymerization temperature from 85 to 115°C decreases grafting. This is rather interesting, since higher initiator concentrations and temperatures favor the termination process, a point which substantiates the above suggestion.

Monomer Concentration

The effect of AA concentration on percent grafting is shown in Figure 2. As is evident, the percent grafting increases by increasing the AA concentration up to 10%. Thereafter, no significant improvement in percent grafting is observed upon further increasing the monomer concentration. It seems that with AA concentrations higher than 10%, a certain amount of graft formation occurs which acts as a diffusion barrier for monomer, initiator, and growing homopolymer chains. As a result, no enhancement is observed when higher concentrations of monomer are used.

To check the validity of the postulate that the initial graft formation acts as diffusion barrier, PET samples polymerized with poly(acrylic acid) at AA concentrations of 5, 10, 20, and 50% were thoroughly washed with boiled water and dried, then dyed with a cationic dye (Methylene Blue). Microscopic examination of these samples revealed (a) that at lower AA concentration (5%), the polymer was located mainly at the surface; (b) that at an AA concentration of 10%, the polymer was distributed throughout the cross sections of the fibers but tended to be more concentrated at their outer surfaces; and (c) that no change in the polymer distribution could be observed by increasing the AA concentration up to 50%. This reflects the role of diffusion interacting with the irreversible polymerization reactions.

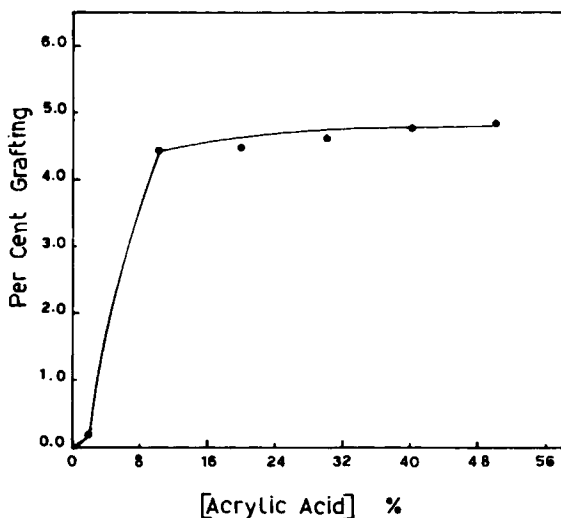


Fig. 2. Effect of acrylic acid concentration on graft yield. $[H_2O_2]$, 100 mequiv/L; reaction time, 4 h; temperature, 85°C; material:liquor ratio, 1:100.

Addition of Metallic Salts

Previous reports^{12,40} have shown that incorporation of metallic salts such as copper sulfate in the vinyl graft polymerization media exerts a considerable influence on the percent grafting. Figure 3 shows the effect of ferrous ammonium sulfate and copper sulfate on grafting AA to PET fibers using H_2O_2 as initiator. It is obvious that the rate and extent of grafting decrease significantly when the polymerization reaction was conducted in the presence of these salts. This indicates that the latter act as free radical traps. Further, the lower rate and extent of grafting found with copper sulfate than ferrous ammonium sulfate imply that the former is a more powerful scavenger than the latter.

Reaction Time

The effect of reaction time on percent grafting is shown in Figure 3. The effect is related to the presence of metallic salts. When the grafting reaction was carried out in the presence of copper sulfate, the percent graft increased by increasing the reaction time, and no leveling off of grafting was observed within the range studied. A similar trend was obtained with grafting in the presence of ferrous ammonium sulfate but grafting did level off after 4 h. In the absence of metallic salts, on the other hand, leveling off of grafting occurs within 1 h. This, indeed, calls for the validity of the suggestion that formation of a certain amount of graft makes it difficult for the grafting reaction to proceed further since this graft formation acts as a diffusion barrier. However, the adverse effect of depletion of concentration of monomer and initiator as well as the decrement in the number of growing homopolymer chains on the percent grafting as the reaction proceeds cannot be ruled out.

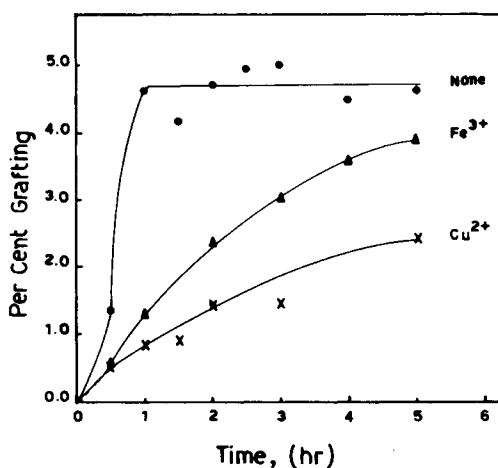


Fig. 3. Rate of grafting of acrylic acid onto PET fibers in presence and absence of salts: (●) none; (▲) ferrous ammonium sulfate; (x) copper sulfate; [AA], 10%; [H_2O_2], 100 mequiv/L; temperature, 85°C; material:liquor ratio, 1:100.

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