H_2O_2-Induced Graft Polymerization of Acrylic Acid/ Styrene Mixtures on Poly(ethylene Terephthalate) Fibers

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Synopsis

Graft polymerization of acrylic acid/styrene mixtures on poly(ethylene terephthalate) fibers using H_2O_2 as initiator was investigated under different conditions including acrylic acid/styrene ratio, monomer mixtures concentration, initiator concentration, polymerization temperature, pH of polymerization medium, addition of metallic salts, and use of solvent/water mixture instead of aqueous medium. It was found that the rate and extent of grafting for acrylic acid/styrene mixtures were much higher than those of single monomers, indicating a synergestic effect. Maximum percent grafting occurred when acrylic acid/styrene mixture at a ratio of 30:70 was used. Increasing the monomer mixture concentration from 2% to 40% was accompanied by a significant enhancement in percent grafting. The latter increased also significantly as the H_2O_2 concentration increased from 10 to 150 meq/L; a further increase in H_2O_2 concentration decreased grafting. No grafting took place at 65°C even after 4 h. Raising the polymerization temperature to 75°C expedited grafting; the magnitude of the latter increased by increasing the temperature up to 95°C. Addition of copper sulphate and ferrous ammonium sulphate to the polymerization system offset grafting, the opposite holds true for lithium chloride provided that its concentration does not exceed 15 mmole/L. Methyl alcohol/water mixture (20:80) constituted the optimal medium for polymerization. Grafting of acrylic acid/styrene mixtures to poly(ethylene terephthalate) fibers resulted in considerable improvement in moisture regain of the latter.

INTRODUCTION

Grafting of polyester fibers with styrene,[1-6] 4-vinyl pyridine,[7,8] acrylonitrile,[9-12] acrylic and methacrylic acids,[13-16] glycidyl methacrylate,[17] vinyl acetate,[18] *N*-vinyl-3-morpholinone,[19] and 2-methyl-5-vinylpyridine,[20-22] using physical and chemical means for initiation has been reported. Previous reports[23] have also dealt with grafting of mixtures of styrene with methyl acrylate, 4-vinyl pyridine, or acrylonitrile on low density polyethylene as well as mixtures of styrene with methyl methacrylate or acrylonitrile on wool.[24] It is suggested that if this comonomer procedure is used for grafting, and if styrene is one of the monomers involved, competing homopolymerization is decreased and efficient grafting is readily achieved.[24]

In this work, graft polymerization of acrylic acid/styrene mixtures on poly(ethylene terephthalate) fibers using H_2O_2 as initiator was investigated. The polymerization reaction was carried out under different conditions to find out the main factors affecting the reaction. In addition, moisture regain of the grafted product was examined.

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EXPERIMENTAL

Materials

Poly(ethylene terephthalate) fibers (PET) were purified by washing with hot and cold water, dried at room temperature, and finally extracted with methyl alcohol for 24 h.

Acrylic acid and styrene were freed from the inhibitors by vacuum distillation.

Hydrogen peroxide (Merck), copper sulphate ($CuSO_4 \cdot 5H_2O$), and ferrous ammonium sulphate ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$), and lithium chloride (LiCl) were of analytical grade chemicals.

Methyl alcohol, isopropyl alcohol, benzyl alcohol, 1,1,2,2-tetrachloroethane were of pure grade chemicals.

Polymerization Procedure

The polymerization reaction was carried out in a 100-mL stoppered conical flask, PET fiber (0.5 g) was introduced into a 50-mL aqueous solution containing the monomers. 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, washed with water, and washed several times with benzene and with a mixture of benzene methyl alcohol (50:50) and boiled with water three times, the sample was then Soxhlet extracted with (1:1) mixture of benzene:methyl alcohol, dried in an oven at 105°C for 5 h, cooled to room temperature, and weighed. The increase in weight of the sample divided by its original dry weight and multiplied by 100 will be referred to as percent grafting:

$$\%\ \text{grafting} = \frac{(\text{dry wt grafted sample}) - (\text{dry wt original sample})}{\text{dry wt original sample}} \times 100$$

$$\%\ \text{homopolymer} = \frac{\text{dry wt of homopolymer}}{\text{wt of monomer used}} \times 100$$

Determination of Structure of Poly(acrylic Acid/Styrene) Grafted to PET

The structure of the copolymer using mixtures of acrylic acid and styrene was monitored by analysis of the carboxyl content. The latter was determined as follows: the accurate weight of PET grafted with a mixture of acrylic acid and styrene was impregnated in $0.1N$ HCl over night. The sample was then washed thoroughly with distilled water till free of the acid. At this end the sample was dissolved in a 100-mL phenol/tetrachloroethane mixture (50:50) followed by potentiometric titration against $0.05N$ NaOH till pH = 7. A blank experiment was carried out in which pure PET dissolved in 100 mL of the phenol/tetrachloroethane mixture was similarly titrated against $0.05N$ NaOH.

$$\text{Carboxyl content} = \frac{(V - V') \times N \times 0.045 \times 100}{W}$$

V = amount of NaOH in presence of grafted fiber (mL)
V' = amount of NaOH in presence of pure fiber (mL)
N = normality of NaOH
W = weight of the fiber used (g).

RESULTS AND DISCUSSION

Figure 1 shows the rate of grafting of acrylic acid, styrene, and their binary mixtures at a ratio of 60:40 onto PET fibers using H_2O_2 as initiator. Obviously, the grafting reaction exhibits an induction period irrespective of the monomer used. Nevertheless, the induction period observed with acrylic acid is longer than for a styrene and acrylic acid/styrene mixtures. While the induction period for acrylic acid amounts to about 45 min, it amounts to about 15 min for both styrene and acrylic acid/styrene mixtures. The induction period could possibly be attributed to the lower diffusion of monomer solution into the fiber or to the presence of traces of impurities in the monomer which could react with the radicals initially produced by decomposition of H_2O_2 in the presence of PET fibers. Hence the difference in the induction period between grafting acrylic

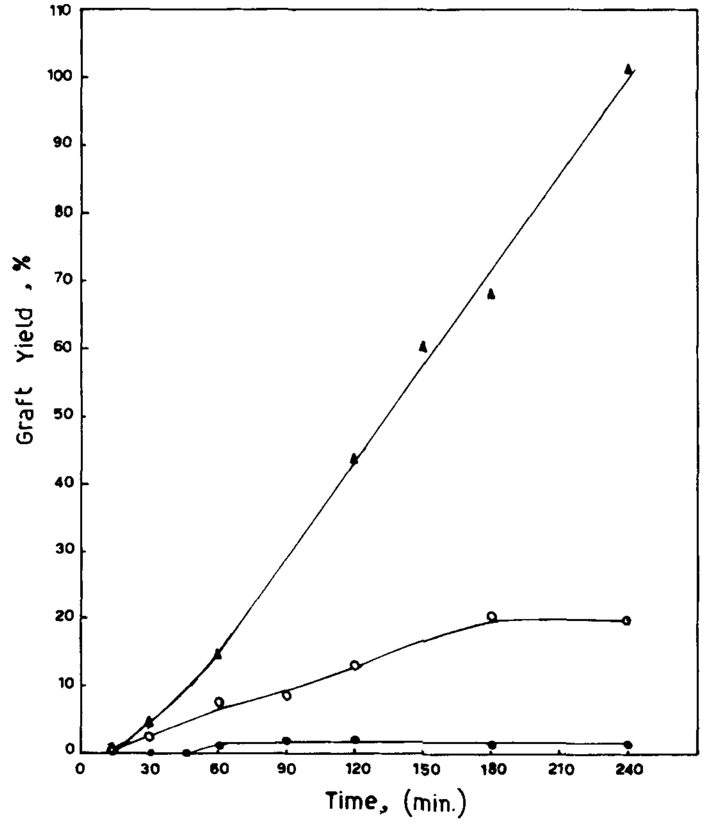

Fig. 1. Rate of grafting of acrylic acid, styrene, and their binary mixtures (60:40) onto PET fibers. (●) Acrylic acid; (○) styrene; (▲) acrylic acid/styrene mixture; [monomer], 20%; [H_2O_2], 100 meq/L; temperature = 85°C; material:liquor ratio = 1:100.

acid and grafting styrene or acrylic acid/styrene mixtures would suggest that the diffusion of styrene-containing solution into PET fibers is higher than acrylic acid solution.

It is also seen (Fig. 1) that the extent and rate of grafting of acrylic acid are significantly lower than those of styrene and acrylic acid/styrene mixtures. Furthermore, the very low grafting obtained with acrylic acid could be due to preferential homopolymer formation. In favor of and in combination with this are the low diffusion of acrylic acid into and affinity for PET fibers, which, in turn, would be reflected on its reaction with PET macroradicals. Using styrene as comonomer during grafting of acrylic acid enhances grafting significantly. As is evident (Fig. 1), the rate and extent of grafting for acrylic acid/styrene mixtures (at a ratio of 60:40) are much higher than those of single monomers, indicating a synergistic effect.[25] For instance, percent grafting of 1.5%, 19.2%, and 101.4% could be achieved after 4 h upon using acrylic acid, styrene, and acrylic acid/styrene mixture, respectively.

Acrylic Acid/Styrene Ratio

It has been shown above that if acrylic acid/styrene mixture at a ratio of 60:40 is used as a comonomer, significant grafting takes place. Variation of the percent grafting with changing the ratio of each monomer in the comonomer mixture is shown in Figure 2. It is clear that maximum percent grafting occurs when acrylic acid/styrene mixture at a ratio of 70:30 was used. Below or above this ratio results in decreased grafting. However, the percent grafting for the monomer mixtures is higher than that obtained with acrylic acid regardless of the acrylic acid/styrene ratio in the monomer mixtures. The same situation is encountered when the percent grafting for the monomer mixtures is compared with that of styrene except in mixtures having acrylic acid/styrene ratio 95:5. With the latter mixture the percent grafting is lower than that of styrene.

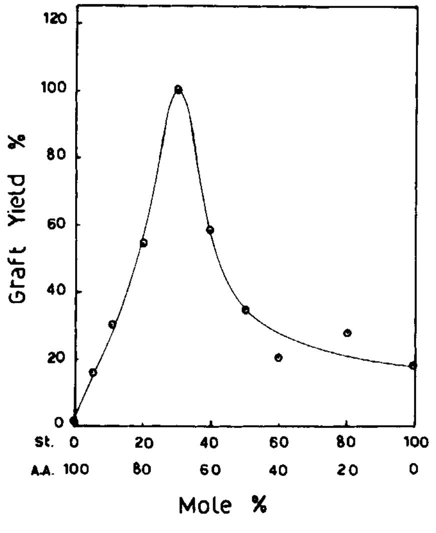

Fig. 2. Variation of the percent grafting with changing the ratio of acrylic acid and styrene in the comonomer mixtures. Monomer concentration, 20%; [H_2O_2], 100 meq/L; temperature = 85°C; reaction time = 4 h; material:liquor ratio = 1:100.

In short, using styrene (up to 40 mol % in the monomer mixtures) as a comonomer in grafting of acrylic acid to PET fibers enhances the percent of grafting of acrylic acid. The same holds true for styrene provided that the ratio of acrylic acid in its binary mixtures with styrene does not exceed 95:5. Acrylic acid/styrene mixture at a ratio of 70:30 constitutes the optimal since at this ratio the percent grafting is significantly higher with the monomer mixture than with single monomers.

Based on the above, it is probably correct to say (a) that there is a synergistic effect when mixtures of styrene and acrylic acid are grafted to PET fibers, (b) that the magnitude of this synergistic effect depends upon the acrylic acid/styrene ratio in the monomer mixtures, (c) that the synergistic effect is more pronounced at acrylic acid/styrene ratio of 70:30, and (d) that the use of styrene as a comonomer in grafting of acrylic acid to PET activates the acrylic acid monomer and makes it more amenable to grafting (cf. Table I).

Monomer Mixture Concentration

The effect of acrylic acid/styrene mixture (60:40) concentration on percent grafting is shown in Figure 3. The effect of the concentration of single monomer on percent grafting is shown in the same figure for comparison. It is seen that increasing the monomer mixture concentration from 2% to 40% is accompanied by a significant enhancement in percent grafting. A similar trend was observed when the concentration of styrene was increased up to 30%, but further increase in styrene concentration leaves the percent grafting practically unaltered. With acrylic acid, on the other hand, no grafting occurs below a concentration of 10%. Furthermore, increasing the acrylic acid concentration from 10% to 40% causes no significant improvement in percent grafting, which is obviously very low.

A comparison between the effect of monomer mixture concentration with that of single monomers would indicate that the percent grafting for the monomer mixture is considerably higher than single monomers irrespective of the concentration used (Fig. 3). This suggests (a) that the monomer mixture acquires

TABLE I
Contribution of Acrylic Acid in Poly(acrylic Acid/Styrene) Grafted to PET Fibers

Molar ratio of monomers used		Graft yield	Structure of poly(AA/St) copolymer			
			(wt %)		mol %	
AA[a]	St[b]	(%)	AA[a]	St[b]	AA[a]	St[b]
100	—	1.5				
95	5	16.6	24.30	75.70	31.69	68.31
90	10	31.2	14.23	85.77	19.33	80.67
80	20	55.0	7.35	92.65	10.28	89.72
70	30	101.4	3.65	96.35	5.18	94.82
60	40	59.2	4.26	95.74	6.03	93.97
50	50	35.6	4.55	95.45	6.44	93.56
40	60	20.8	4.13	95.87	5.85	94.15
20	80	28.4	2.75	97.25	3.92	96.08
—	100	19.2				

[H_2O_2], 100 meq/L; temperature = 85°C; time = 4 h; material:liquor ratio = 1:100.

[a] AA = acrylic acid.

[b] St= styrene.

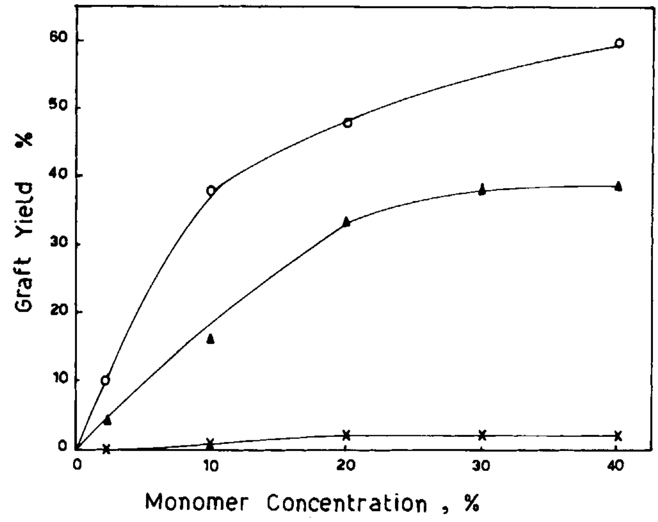

Fig. 3. Effect of concentration of acrylic acid, styrene, and acrylic acid/styrene mixture (60:40) on percent grafting. (X) Acrylic acid; (▲) styrene; (O) acrylic acid/styrene mixture (60:40); [H_2O_2], 100 meq/L; temperature = 85°C; reaction time = 4 h; material:liquor ratio = 1:100.

higher affinity to PET fibers than single monomers, (b) that the monomer mixture improves the swellability of PET fibers, (c) that the competing homopolymerization is decreased (data in Table II support this), and (d) that the termination of growing polymer chain radicals and/or PET macroradicals proceeds in much slower rates in case of monomer mixture than single monomers.

Figure 4 shows the rate of grafting at different monomer mixture concentrations. The monomer mixture consisted of acrylic acid/styrene at a ratio of 60:40. It is seen that, regardless of the monomer mixture concentration used, grafting increases significantly by increasing the reaction time, particularly when a monomer mixture concentration higher than 2% was used. However, the grafting reaction shows the induction period, the value of which depends upon the monomer mixture concentration. The higher the concentration, the shorter the induction period becomes. The induction period amounts to 60 min when 2% monomer mixture concentration was used. This contrasts with an induction period of 15 min at a monomer mixture concentration of 20%. This suggests that swelling of PET fibers is favored at higher monomer mixture concentration, thus

TABLE II
Homopolymer Formed During Graft Polymerization of Acrylic Acid/Styrene Mixture to PET Fibers

Monomer concentration (%)	Homopolymer (%)		
	Acrylic acid	Styrene	Acrylic acid/ styrene mixture (60:40)
10	199.64	2.20	40.71
20	131.28	6.00	51.56
40	105.16	6.00	62.45

[H_2O_2], 100 meq/L; temperature = 85°C; time = 4 h; material:liquor ratio = 1:100.

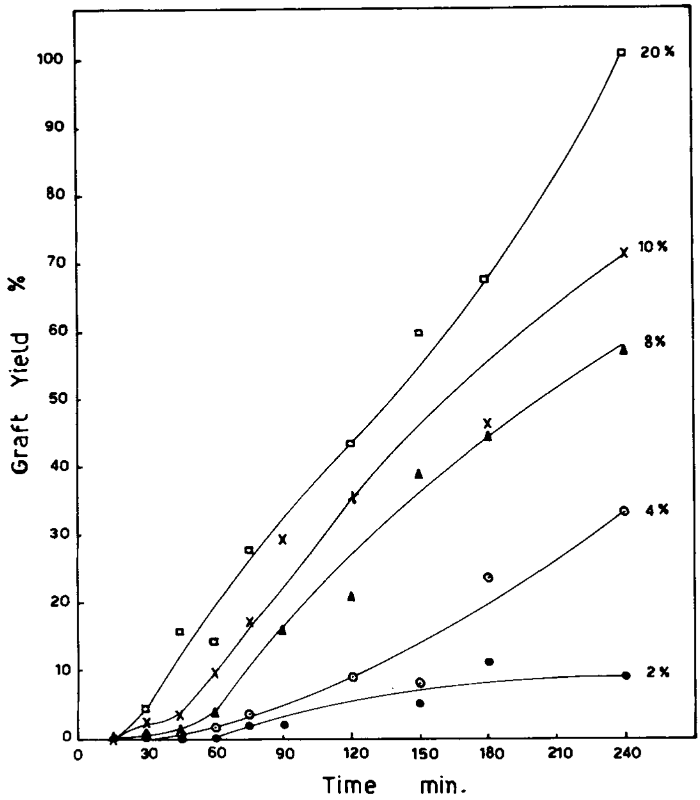

Fig. 4. Rate of grafting of acrylic acid/styrene mixture (60:40) at different concentrations onto PET. [Acrylic acid/styrene mixture], %: (●) 2; (⊙) 4; (▲) 8; (×) 10; (□) 20; [H_2O_2], 100 meq/L; temperature = 85°C; material:liquor ratio = 1:100.

facilitating diffusion of both monomer and initiator. Decomposition of the latter would take place in close proximity of PET structure where the monomer mixture would be available. As a result, the induction period is shortened.

Initiator Concentration

Figure 5 shows the effect of H_2O_2 concentration on percent grafting on PET fibers when acrylic acid/styrene mixture (60:40) at a concentration of 20% was used. Evidently, the percent grafting increases significantly as the H_2O_2 concentration increases from 10 to 150 meq/L. Further increase in H_2O_2 concentration decreases the percent grafting.

The enhancement of grafting by increasing H_2O_2 concentration to a certain limit implies that the hydroxyl radicals formed via decomposition of H_2O_2 in the polymerization system participate essentially in initiation of grafting. Above this limit, the abundance of hydroxyl radicals leads to participation of these radicals in the termination of the growing polymer (grafted chains and PET macroradicals) as well as to the combination of hydroxyl radicals, thereby giving rise to decreased grafting.

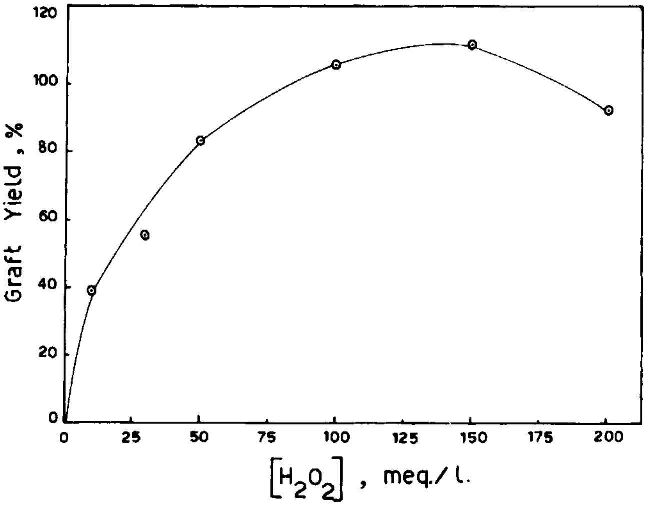

Fig. 5. Effect of initiator concentration on percent grafting. [Acrylic acid/styrene mixture], 20%; temperature = 85°C; reaction time = 4 h; material:liquor ratio = 1:100.

Polymerization Temperature

Figure 6 shows the effect of polymerization temperature on grafting acrylic acid/styrene mixture (60:40) to PET fibers. It is observed that no grafting occurs at 65°C even after 4 hr. Raising the polymerization temperature to 75°C brings about substantial amount of graft formation. Nevertheless, an induction period of 2 h is noticed. Increasing further the polymerization temperature to 85°C is accompanied by significant improvement in grafting and reduction in the induction period. The latter amounts only to 15 min. Carrying out the graft polymerization temperature at 95°C causes further enhancement in grafting, and no induction period is noticed.

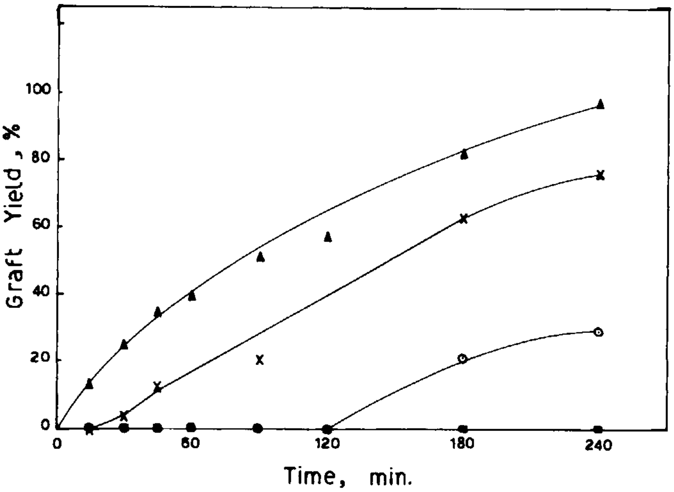

Fig. 6. Effect of polymerization temperature on grafting acrylic acid/styrene mixture (60:40) to PET fibers. [Acrylic acid/styrene mixture], 20%; $[H_2O_2]$, 100 meq/L; (■) 65°C; (⊙) 75°C; (X) 85°C; (▲) 95°C; material:liquor ratio = 1:100.

The enhancement of grafting by raising the polymerization temperature could be associated with the favorable influence of the latter on: (a) swellability of the PET fiber, (b) miscibility and mobility of the monomer mixture and the effect of these on swelling properties of the PET fibers, (c) diffusion of both monomer mixture and initiator into the PET fiber, (d) decomposition of H_2O_2 to produce hydroxyl radicals, and (e) initiation and propagation of the graft. It was often observed that rising the polymerization temperature decreases grafting due to the fast rate of termination,[20,22] which is in contrast to current work. This reflects differences in the nature of monomers and their susceptibility of the termination process.

pH of Polymerization Medium

The effect of pH of the polymerization medium on grafting acrylic acid/styrene mixtures (60:40) to PET fibers is shown in Figure 7. Evidently, the percent grafting decreased significantly when the pH was increased from 2 to 6 and no grafting occurred at pH = 8. This indicates that grafting is only favored in relatively high acidic media and is offset in alkaline media.

That grafting occurs only in polymerization media of low (acidic) pH's and is completely inhibited in alkaline media signifies the role of the pH of the polymerization media on the mode of interaction of acrylic acid/styrene mixture with PET fibers. It seems that decomposition of H_2O_2 in the presence of PET fibers and the monomer mixture in question, yielding hydroxyl radicals capable of initiating grafting, is favored in acidic medium. Similarly, swelling of PET fibers by the monomer mixture and miscibility of the latter are also favored at acidic pH's. Consequently, grafting is achieved in acidic media. At alkaline pH's, on the other hand, the reverse seems to be the case. H_2O_2 decomposes to yield nascent oxygen. The latter is well known with its inhibition effect on polymerization.[22] Furthermore, conversion of the acrylic acid, in the monomer mixture, to its sodium salt would certainly have an adverse effect on its miscibility

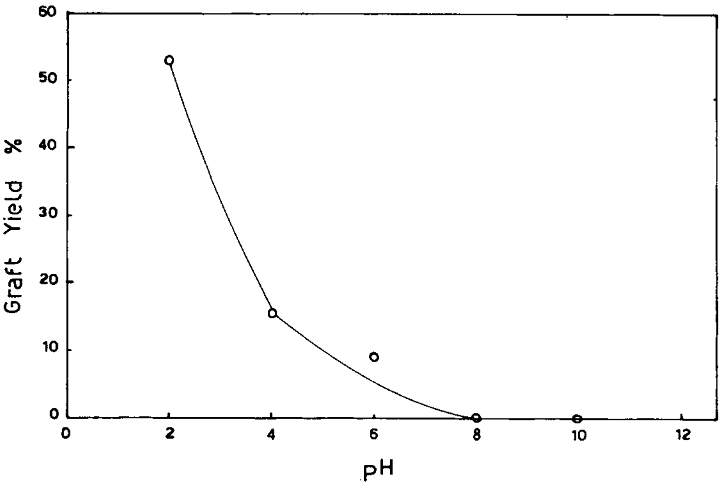

Fig. 7. Effect of pH of the polymerization medium on percent grafting. [Acrylic acid/styrene mixture], 20%; [H_2O_2], 100 meq/L; temperature = 85°C; reaction time = 4 h; material:liquor ratio = 1:100.

and reactivity. Hence immiscibility and, therefore, low reactivity as well as formation of oxygen would account for ceasing grafting in alkaline medium.

Addition of Metallic Salts

Addition of metallic salts such as ferrous ammonium sulphate and copper sulphate to the vinyl system has been reported to have a considerable influence on the magnitude of grafting on various textile fibers.[20,26–30] Figure 8 shows the variation in percent grafting on PET fibers, obtained with acrylic acid/styrene mixtures (60:40), using H_2O_2 as initiator, with metallic salt concentration. Three metallic salts were independently used, namely, copper sulphate, ferrous ammonium sulphate, and lithium chloride. It is observed that the percent grafting diminishes when traces of copper sulphate or ferrous ammonium sulphate are incorporated in the polymerization system. Addition of these two salts at concentration above 5 mmol/L offsets grafting completely. This indicates that the cupprous ions and ferrous ions act as a radical trap, confirming previous reports.[20,21]

With lithium chloride, on the other hand, considerable enhancement in percent grafting is achieved provided that the lithium chloride concentration does not exceed 15 mmol/L. Above this concentration, the percent grafting tends to decrease. The implication of this is that presence of lithium chloride up to a certain concentration in the polymerization system helps decomposition of H_2O_2 to yield efficient hydroxyl radicals for grafting. At relatively high lithium chloride concentration, the lithium ions seem to participate in the termination of growing grafted chain radicals and PET macroradicals. Stated in other words, low concentration of lithium ions favors graft initiation, thereby leading to higher grafting, whereas high concentration decreases grafting by participation of lithium ions in termination processes.

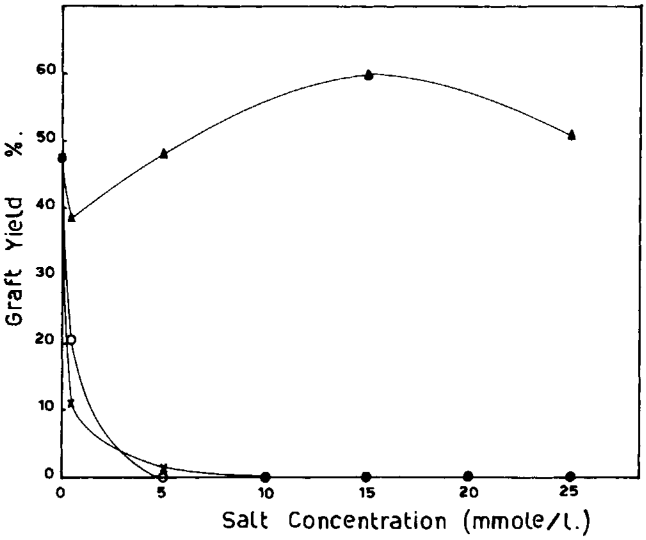

Fig. 8. Effect of metallic salts concentration on percent grafting. [Acrylic acid/styrene mixture], 20%; [H_2O_2], 100 meq/L; (○) $CuSO_4 \cdot 5H_2O$; (×) $FeSO_4 \cdot (NH_4)_2SO_4$—$6H_2O$; (▲) LiCl; temperature = 85°C; reaction time = 4 h; material:liquor ratio = 1:100.

Polymerization Medium

The graft polymerization reaction of acrylic acid/styrene mixtures (60:40) was carried out, as described in the experimental section but in solvent/water mixture instead of the aqueous medium. Methyl alcohol, isopropyl alcohol, benzyl alcohol, and tetrachloroethane were independently used at different ratios as the solvent. The results obtained are shown in Figure 9. It is seen that using a solvent/water mixture at ratios of 2:98 and 4:96 as a polymerization medium decreases grafting regardless of the solvent used.

The effect of the nature of the solvent becomes apparent at a higher solvent/water ratio. For example, gradual variation of the ratio of methyl alcohol from 5:95 up to 20:80 in the solvent/water mixture causes a considerable enhancement in percent grafting. Further increase in methyl alcohol ratio decreases grafting. The same situation is encountered when isopropyl alcohol was used instead of methyl alcohol and upon raising isopropyl/water ratio from 10:90 up to 20:80. However, the improvement in grafting observed with methyl alcohol is much higher than isopropyl alcohol. This suggests that methyl alcohol/water mixture (20:80) is more capable of swelling PET fibers in presence of acrylic acid/styrene mixture than the corresponding isopropyl alcohol/water mixture. Once this is the case, diffusion of the monomer mixture as well as the initiator will be facilitated, thereby giving rise to increased grafting.

In contrast with methyl alcohol and isopropyl alcohol, using benzyl alcohol/water or tetrachloroethane/water at a ratio of 20:80 diminishes grafting significantly. Indeed, with the latter mixture, grafting is inhibited completely.

Based on the foregoing, it may be stated that grafting acrylic acid/styrene mixtures (60:40) to PET fibers is considerably influenced by the medium of polymerization. Carrying out the latter in solvent/water mixture instead of aqueous medium changes the magnitude of grafting. Methyl alcohol/water mixture (20:80) constitutes the optimal medium for polymerization. Replacing methyl alcohol with isopropyl alcohol in this mixture leads to higher grafting as compared to aqueous medium but less than methyl alcohol/water mixture.

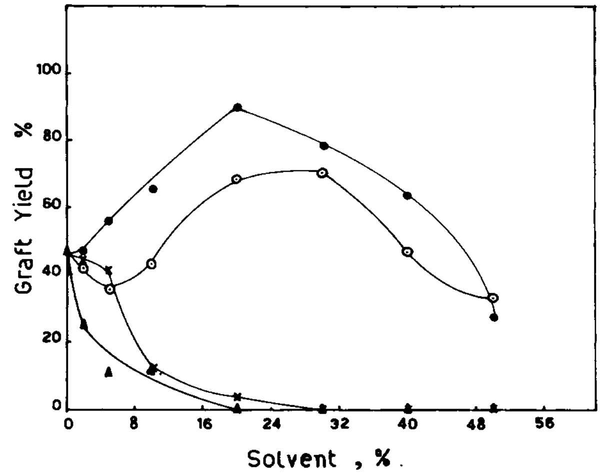

Fig. 9. The effect of solvent % on percent grafting. [Acrylic acid/styrene], 20%; [H_2O_2], 100 meq/L; (●) methyl alcohol; (⊙) isopropyl alcohol; (×) benzyl alcohol; (▲) tetrachloroethane; temperature = 85°C; reaction time = 4 h; material:liquor ratio = 1:100.

TABLE III
Effect of Grafting of PET Fibers with Acrylic Acid, Styrene, and Acrylic Acid/Styrene Mixtures on Moisture of Fibers

	% Grafting	Moisture regain (%)
Nongrafted PET	—	0.300
PET grafted with acrylic acid	1.66	0.454
PET grafted with styrene	19.2	0.370
PET grafted with acrylic acid/styrene mixtures (60:40)	3.60	0.349
	4.40	0.570
	14.80	0.932
	28.00	1.009
	60.00	1.182
	101.14	1.663

The opposite holds true for benzyl alcohol/water and tetrachloroethane/water mixtures wherein grafting is offset, particularly at higher solvent ratio in the mixture.

Differences in the magnitude of grafting by using various solvent together with water as a polymerization medium could be traced back to differences in (a) the ability of the solvent to swell PET fibers, (b) miscibility with monomer mixture, (c) formation of solvent radical from the primary radical species of the initiator, (d) contribution of the solvent radical in activation of PET, and (e) participation in the termination of free radicals in the polymerization medium as well as PET and on growing grafted chain transfer. While the first four factors favor grafting by simplifying access and diffusion of the monomer, the last factor adversely affects grafting by lowering the molecular size of the graft.[20]

Moisture Regain

Table III shows the moisture regain of PET fibers before and after grafting with acrylic acid/styrene and their binary mixtures. It is seen that there is a substantial improvement in moisture regain after grafting with acrylic acid. The same holds true for PET grafted with acrylic acid/styrene mixtures. This could be associated with hydrophilization of the PET by the polymer-containing carboxylic groups. Besides this, propping apart of the surfaces of the PET elementary fibrils by the grafted polymer would lead to a more open internal structure, thereby facilitating accommodation of water. This is rather substantiated by the findings that polystyrene—PET graft copolymer acquires higher moisture regain than PET despite the hydrophobic nature of polystyrene and that the moisture regain increases by increase in the percent grafting for acrylic acid/styrene mixture on PET.

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