

## Grafting on Polyester Fibers

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### Synopsis

Acrylic acid (AA) and acrylonitrile (AN) were used to carry out grafting on polyester (PE) fibers using the techniques of initiation by  $\gamma$ -radiation as well as benzoyl peroxide. The nature of the grafted fiber substance was found to be the same, irrespective of the grafting technique. Extent of grafting depended upon the time, concentration of the initiator, and the monomer as well as on the irradiation dose. The increase in the moisture regain was directly proportional to the amount of graft in the fiber. AA grafted fibers were rendered more hydrophilic than AN grafted fibers for equivalent amount of grafts. Considerable improvement in dyeability of the PE fibers was possible through grafting. About 50% to 100% improvement with disperse dyes was observed in case of PE fibers containing 22.4% and 9.0% graft of AA and AN, respectively. Intense fast dyeing with direct and basic (cationic) dyes was also possible, and the dye content was proportional to the extent of graft introduced in the fiber. The CN groups were reduced to  $\text{NH}_2$  groups in the AN graft on the fiber. In this way, deep, fast, and bright dyeing was obtained with reactive dyes. Electrokinetic studies were carried out on the grafted fibers. With the increased amount of AA graft, the maxima in the zeta potential curve shifted toward higher acidic pH as greater amounts of alkali was utilized by the  $-\text{COOH}$  groups in the graft. In this respect, CN groups were less sensitive due to their lesser polarity as compared to the carboxylic groups. It was observed from surface charge density (S.C.D.) studies that the effective surface area of the fiber decreased with the increase in the amount of graft, particularly in case of AN graft. Surface conductivity (S.C.) studies revealed that with increase in the number of polar groups ( $-\text{COOH}$ ) on the surface of the fiber, the S.C. increased with the increase in the amount of AA graft. In case of AN grafts, the reduction in effective surface area of the fiber played a more important role than the contribution by the CN groups to surface conductivity.

### INTRODUCTION

Poly(ethylene terephthalate) fibers are highly crystalline, markedly hydrophobic, and do not contain chemically reactive groups. Hence, this material is not easily penetrated by dyes of large molecular dimensions and cannot combine with dye anions or cations. Certain desirable properties (e.g., dyeability with basic, direct, and other classes of dyes; improvement in antistatic properties; increase in moisture regain, etc.) can be imparted to poly(ethylene terephthalate) by grafting it with monomers just as acrylic acid, acrylonitrile, 4-vinylpyridine, acrylamide, etc.

Grafting of a monomer on to a polymer can be accomplished either by radiation or chemical means. Ionizing radiations like  $\gamma$ -rays from a cobalt 60 source or high-energy electrons from accelerators interact with the polyester fiber (PE) and produce radicals one of which was identified by ESR<sup>1</sup> as  $-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{O}-\dot{\text{C}}\text{H}-\text{CH}_2-$ . These radical sites permit the attachment of monomer molecules which may grow into short chains. Grafting can be accomplished either by directly irradiating the fiber with the monomer or by first creating a radical site and then adding the monomer.

In the chemical method, the active site can be created by oxidizing the polymer to hydroperoxide<sup>2-6</sup> at several points along the chain in a random manner and then allowing it to decompose into the active form in presence of the monomer either by heat or by a redox system. Suzuki and co-workers<sup>7</sup> carried out the grafting of vinyl monomers on to PE by ceric sulfate in nitrogen atmosphere. The same result can be obtained by adding a free-radical initiator.

Stannet and co-workers<sup>8-11</sup> studied various aspects of radiation grafting on polymers extensively. Sakurada and Kawahara<sup>12</sup> studied the poly(ethylene terephthalate)-styrene copolymerization and from the chemical structure found a low degree of grafting of styrene, which was attributed to low sensitivity of polyester to irradiation.

In both the radiation and chemical methods of grafting, the homopolymer of the vinyl monomer is also to be expected but often can be suppressed by suitable additives.<sup>13-16</sup>

The aim of the present investigation was to study the graft copolymerization of acrylic acid and acrylonitrile on to poly(ethylene terephthalate) fibers and fabric by both radiation and chemical methods. Variations in properties such as dyeability, moisture regain, tear strength, and zeta potential of the grafted polyester were evaluated.

## EXPERIMENTAL

### Materials

Polyester fibers (1.5 D  $\times$  1.5 in. KK<sub>2</sub>A) from Chemicals and Fibres of India Ltd. were used for grafting. The fabric used was of Terila, trade mark of Himson India Ltd. woven from 100% polyester filaments. Reagent-grade acrylic acid and acrylonitrile were freed from the inhibitors by vacuum distillation and simple distillation, respectively. The swelling agents, 1,2-dichloroethane and 1,1',2,2'-tetrachloroethane were "chemically pure" grade. Benzoyl peroxide was laboratory grade. The dyes used were Congo Red, Chlorazol Sky Blue FF, and Chrysophenine G (all direct dyes); Duranol Violet 2R and Duranol Red 2R (all disperse dyes); and Astrazon Orange G and Astrazon Orange R (all basic dyes); and were all purified before use.

### Grafting Using $\gamma$ -Rays

The polyester fibers or fabric were swollen in acrylic acid of different concentrations (20% and 50%) and exposed to  $\gamma$ -rays from a cobalt 60 source in the presence of an excess of monomer solution containing 0.01M FeSO<sub>4</sub> to suppress homopolymerization. Per cent graft was varied by varying the conditions of grafting, such as time of swelling, temperature of swelling, and total dose of  $\gamma$ -rays (1–2 Mrad). The homopolymer of acrylic acid was removed by treatment in boiling water for several hours.

### Grafting Using Benzoyl Peroxide

The polyester was first swollen at 90–95°C for 2–3 hr in a solvent-nonsolvent system consisting of either 1,2-dichloroethane/water (20/80 v/v) or tetrachloroethane/water (20/80 v/v). Dichloroethane was removed from the fiber completely by treatment with boiling water. Tetrachloroethane was removed by treatment first with boiling alcohol and then with boiling water. The swollen fibers were used for grafting.

In the case of acrylic acid, 1 g of the fiber was added to a solution containing 0.5 g benzoyl peroxide in 10 ml benzene diluted with 80–90 ml water and 10 ml 50% monomer. For acrylonitrile, the solution contained 0.05–0.15 g benzoyl peroxide in 5–10 ml acetone and 80–90 ml water to which 4 ml monomer and 1 g fiber were added. The grafting was carried out at 70–73°C for 4–8 hr. After the completion of reaction, the fibers were thoroughly washed with boiling water, and the homopolymers adhering were removed by extraction with suitable solvents (boiling water in case of acrylic acid polymer and dimethylformamide at 70°C for several hours and boiling water for 4–5 hr for polyacrylonitrile).

The graft copolymers were dried at 105°C for 2 hr and then over P<sub>2</sub>O<sub>5</sub> in a desiccator.

### Determination of Moisture Regain

The samples were conditioned at 75% R.H. at 30°C and weighed. They were oven dried at 105°C for 2 hr and weighed again:

$$\text{M.R.}(\%) = 100 \times \text{difference in weight/weight of the dry sample.}$$

### Determination of Tear Strength

The tear strength of the polyester and grafted polyester was found by using an Impact Tear Tester.

### Dyeing and Determination of Dye Content

The polyester fibers were dyed at 100°C for direct and basic dyes and 135°C for disperse dyes for 1 hr in a Laboratory High-Temperature Beaker Dyeing Machine manufactured by Electronics and Engineering Company, Bombay; M:L.R. 1:50 and per cent shade, 2.5 for direct and basic dyes and

1.0 for disperse dyes. The dyed samples were soaped in 2 g/l. soap solution at 100°C for 15–20 min. In the case of dyeing with direct dyes, addition of common salt was found to be essential.

The dye content of the dyed fibers was found by extracting the dye from a known amount of the fiber with (a) 25% aqueous pyridine or dimethylformamide in the case of direct dyes; (b) chlorobenzene in the case of disperse dyes; and (c) 50% aqueous acetic acid in the case of basic dyes. The extracts were made up to known volume, and the O.D.'s were measured. Using standard solutions of the dyes made up in identical solvents and measuring the optical densities in a Hilger Pattern Biochem Absorptiometer, the dye uptake of the polyester fibers was determined.

### Determination of Zeta Potential

The apparatus for the determination of zeta potential consisted of a 6-liter bottle, mercury manometer, streaming potential cell with two platinum perforated-disc electrodes, two platinum–mercury–copper electrodes, and an inlet valve. The potential difference between the two platinum electrodes was measured on Aplab Digital D.C. Voltometer Type MB1 (accuracy, 1 mV) when the liquid was flowing through the plug. All resistance and conductivity were measured by using Toshniwal's conductivity Bridge Type CLO 01/014.

An accurately weighed amount of fibrous material (about 5 g cut to an average fiber length of about 0.5 cm) was soaked by vigorous agitation in distilled water and kept in distilled water overnight to ensure complete wetting of the fibers. The wetted fibers were uniformly compressed between the two perforated platinum disc electrodes of the streaming potential cell. The two platinum–mercury–copper electrodes were inserted at the two openings of the cell.

Initially, the two copper wires of the platinum–mercury–copper electrodes were connected and the inlet valve was opened. The streaming solution was forced through the plug at the highest pressure drop so as to remove any air bubbles entrapped in the fiber plug. The solution was streamed through the plug until equilibrium conditions were attained. Once equilibrium was attained, the two copper wires of the two platinum–mercury–copper electrodes were disconnected and the streaming potential was measured as a function of pressure difference from 3 cm to 8 cm of Hg by connecting the two perforated platinum electrodes to a millivoltmeter. After noting the streaming potential, the electrodes were connected to the conductivity bridge. Using appropriate resistance in parallel with the cell circuit, the resistance of the plug with the experimental solution was measured.

The resistance and conductivity of the experimental solution left in the 6-liter bottle were measured with a platinum conductivity cell. The cell constant was determined by the standard procedure using 0.02*N* KCl solution.

Knowing the streaming potential, streaming current, and resistance of the plug, zeta potential was calculated by using Helmholtz-Smoluchowski equation

$$\xi = 6.75 \times 10^7 \times \frac{4\pi n \cdot X \cdot E_s}{D \cdot P}$$

where  $\xi$  = zeta potential (mV),  $n$  = viscosity of solution (poise),  $X$  = specific conductivity of the solution in the plug of fibers ( $\text{ohm}^{-1}\text{cm}^{-1}$ ),  $D$  = dielectric constant of the solution,  $P$  = pressure in the cell (cm of Hg), and  $E_s$  = streaming potential (mV).

For univalent electrolytes, surface charge density was calculated from the equation

$$\sigma = \left( \frac{2NKT D}{\pi} \right)^{1/2} \text{Sinh} \frac{e\xi}{2KT}$$

where  $\sigma$  = surface charge density (e.s.u./ $\text{cm}^2$ ),  $N$  = number of cations or anions per cc in bulk of solution,  $K$  = Boltzman constant ( $1.37 \times 10^{-16}$  ergs/degree),  $T$  = absolute temperature,  $D$  = dielectric constant of the solution,  $e$  = electronic charge, and  $\xi$  = zeta potential (mV).

## RESULTS AND DISCUSSION

Radiation grafting has advantages over the chemical methods in that the per cent graft, length of the chain, etc., can be controlled more easily by varying the dose, dose rate, conditions of swelling, and temperature. However, in any attempts at radiation grafting, one should consider the effect of radiation on the backbone of polymer. Polyester is known to undergo crosslinking on irradiation. It was observed that there is an increase in the tensile strength with dose initially followed by a loss in strength as the dose is increased.<sup>17</sup>

When polyester was reacted with ammonia and chlorine in the presence of  $\gamma$ -rays, the number of reactive sites for dye molecules to attach themselves were increased with the result that considerable improvement in the color value of disperse dyes was observed.<sup>18</sup> Robalenski and co-workers<sup>19,20</sup> grafted acrylic monomers such as vinyl pyridine using  $\gamma$ -radiations and obtained better dyeing behavior with acid dyes. At low temperatures of grafting, the grafting is only on the surface, and there is little loss of strength characteristics even for appreciable amounts of graft. However, at higher temperatures of grafting, the graft is uniformly distributed along the entire cross section of the fiber, and considerable loss in strength occurs.<sup>21-23</sup>

Table I shows the dependence of the extent of graft on swelling conditions and radiation dose. It is observed that 20% acrylic acid gives poor graft yield whether it is swollen at room temperature or at 75°C. Hence, all further studies were carried out with 50% acrylic acid. At room temperature of swelling for 50% AA, a longer time of swelling gives higher graft yield. At 75°C, increasing the swelling time from 2 hr to 24 hr does not ap-

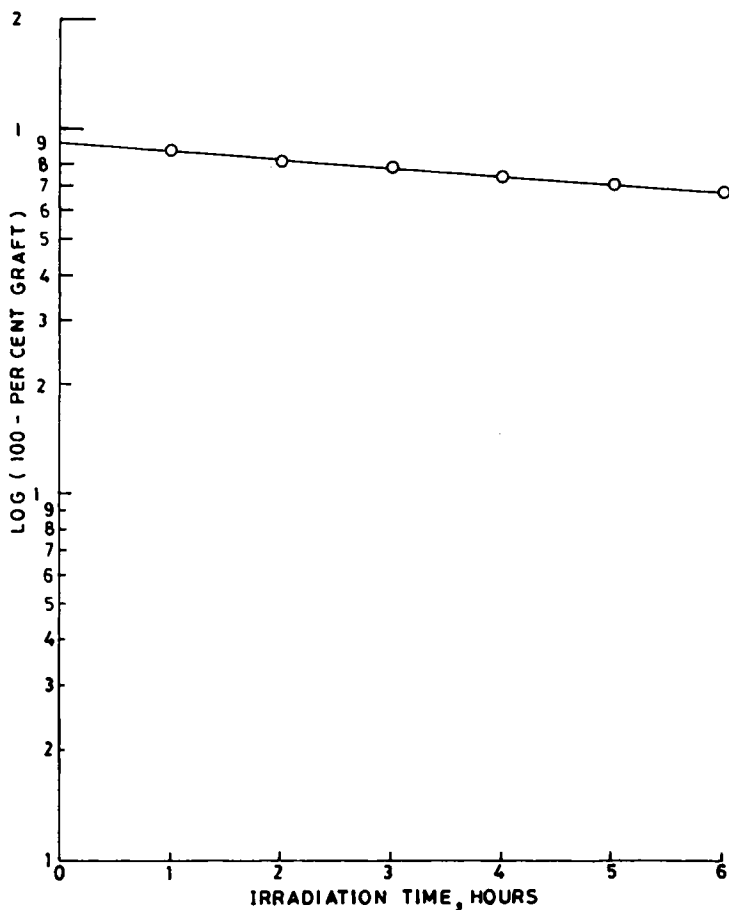


Fig. 1. Log (100-% graft) of acrylic acid on PE fibers vs. irradiation time (hr).

precipably increase the graft yield. These observations lead to the conclusion that for adequate grafting, swelling of the fibers is necessary and that increase of temperature gives an increased rate of swelling and the swelling limit is reached in 2 hr at 75°C. Figure 1 is a plot of  $\log(100\% \text{ graft})$  against time of irradiation, which shows that with increasing dose, graft yield increased and the rate constant for grafting is  $2.56 \times 10^{-3} \text{sec}^{-1}$ . The first-order behavior shows that the rate of grafting is proportional to the concentration of the monomer. However, since (a) saturation grafting is observed even though there is considerable amount of unreacted monomer in the solution phase, (b) the graft yield is independent of fiber-to-solution ratio within certain limits, and (c) even when all the solution is drained out after swelling in acrylic acid solution, the per cent graft obtained is nearly the same as when the fiber is in contact with the solution, it is concluded that the rate of grafting is proportional to the monomer concentration in the swollen

TABLE I  
Effect of Different Parameters on the Amount of Graft of Acrylic Acid on Polyester\*

No.	Swelling conditions	Irradiation time, hr	Graft, %
1	20% AA, swelling at room temperature for 18 hr	4	3.1
2	20% AA, swelling at 75°C for 2 hr	4	3.9
3	50% AA, swelling at room temperature for 24 hr	4	9.7
4	50% AA, swelling at room temperature for 42 hr	4	18.3
5	50% AA, swelling at 55°C for 18 hr	4	26.5
6	50% AA, swelling at 75°C for 2 hr	1	12.2
7	50% AA, swelling at 75°C for 2 hr	2	18.4
8	50% AA, swelling at 75°C for 2 hr	3	20.0
9	50% AA, swelling at 75°C for 2 hr	4	24.2
10	50% AA, swelling at 75°C for 24 hr	4	22.6

\* Dose rate,  $3 \times 10^5$  Rads/hr; temperature of irradiation, 28°C; scavenger,  $\text{FeSO}_4$  M/100.

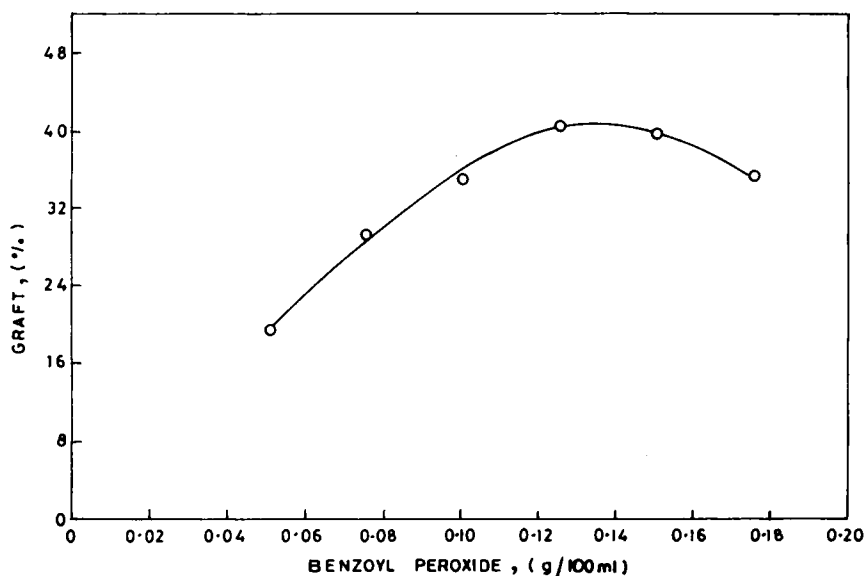


Fig. 2. Per cent acrylonitrile graft vs. benzoyl peroxide (g/100 ml).

phase only and the diffusion of the monomer to the swollen phase during irradiation is negligible.

Figures 2 and 3 show respectively the percentage of acrylic acid and acrylonitrile graft obtained versus the concentration of benzoyl peroxide in solution. The optimum temperature for grafting was found to be 70–73°C. Maximum grafting of 8.3% was observed in the case of acrylic acid at 0.5% benzoyl peroxide concentration and of 40% in the case of acrylonitrile at

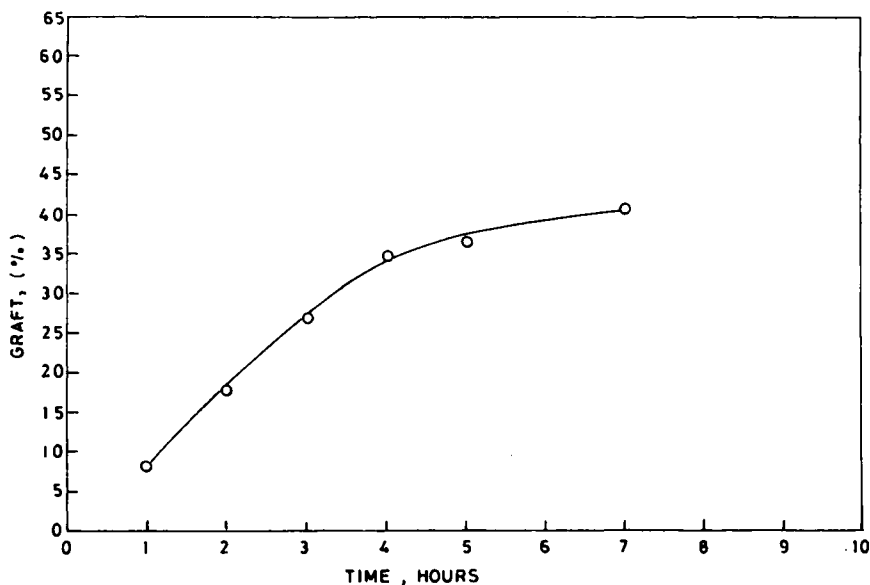


Fig. 3. Per cent acrylonitrile graft vs. time (hr) in benzoyl peroxide.

0.125% benzoyl peroxide concentration. When the concentration of benzoyl peroxide was increased beyond this maximum point, homopolymerization rate increased and there was a decrease in the graft yield.

## EVALUATION OF THE PROPERTIES OF THE GRAFTED SAMPLES

### Strength Characteristics

The results of this study show that there is a considerable decrease in the strength of polyester fabric grafted with acrylic acid by  $\gamma$ -rays, as shown in Figure 4. For example, for 22.4% graft, there was 35% decrease in strength. This decrease is partly due to chain scission and partly to the brittle nature caused by the crosslinking of polyester chains which is known to occur predominantly.<sup>17,18</sup>

### Moisture Regain Characteristics

Polyester fibers are highly hydrophobic in nature, and the moisture content of the fiber is extremely low under normal conditions of temperature and humidity, the value being in the range of 0.4–0.6%. Grafting with acrylic acid not only brings about the opening of the structure to a certain extent but also increases hydrophilicity of the fiber as a result of the introduction of the polar groups, i.e., carboxyl groups in the fiber structure. This shift toward hydrophilic nature is responsible for the increase in moisture regain from 0.6% to 4.46% as the graft percentage of acrylic acid is increased steadily up to 25.6%. These data for the radiation-grafted



fiber as well as from the chemically grafted fiber are shown in Figure 5. Since both sets of data fall on a common curve, it is concluded that the nature of the grafts in both radiation and chemical methods are essentially the same.

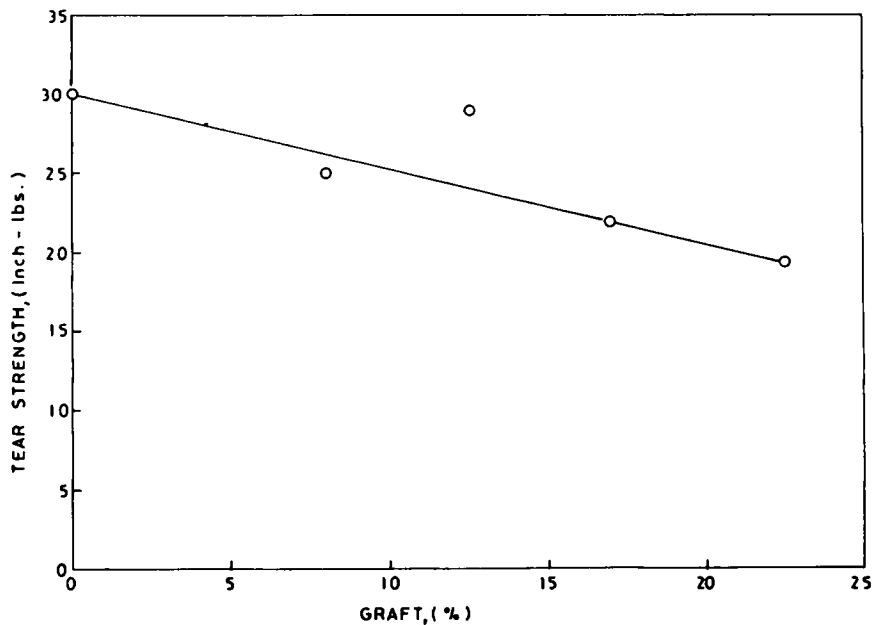


Fig. 4. Tear strength (in.-lb) vs. % graft of AA.

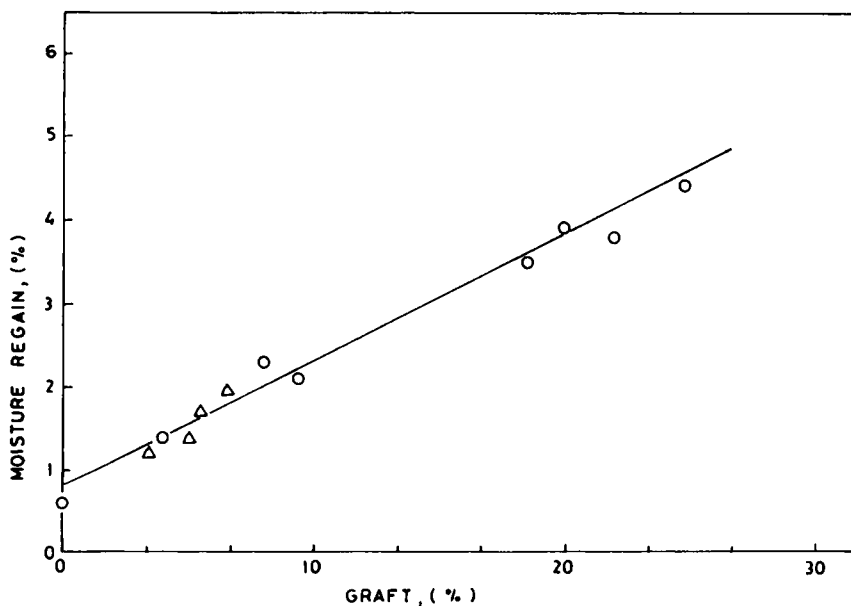


Fig. 5. Moisture regain (%) of acrylic acid-grafted PE fibers: (O) irradiation method; ( $\Delta$ ) benzoyl peroxide method.

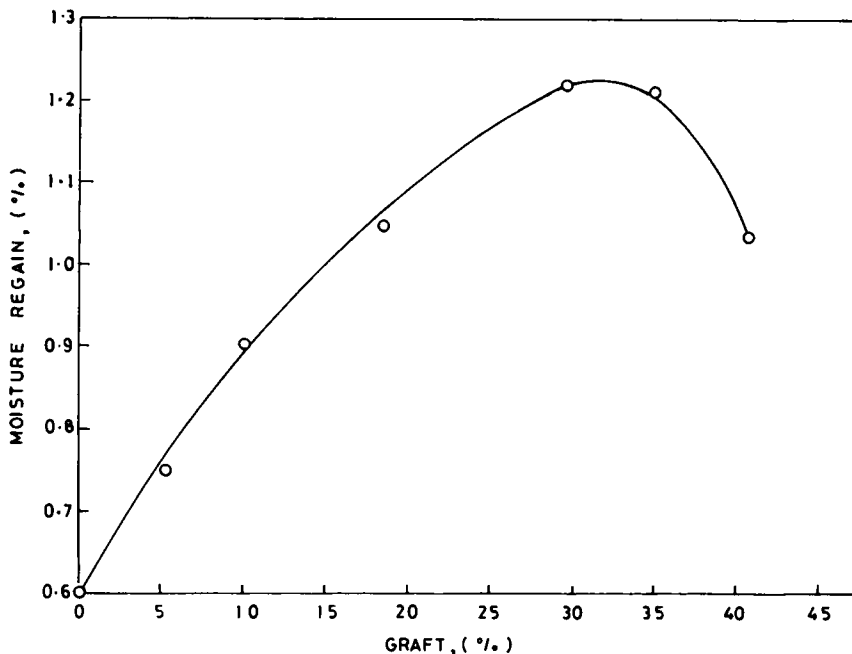


Fig. 6. Moisture regain (%) of acrylonitrile-grafted PE fibers.

In the case of acrylonitrile-grafted polyester, although a similar behavior was observed (Fig. 6), the increase in moisture regain is not as great as in the case of acrylic acid. The maximum moisture regain was only 1.22% (for a 30% acrylonitrile graft), and this low value can be explained as due to the lesser hydrophilic nature of acrylonitrile compared to that of acrylic acid. The decline in moisture regain values beyond 30% grafting is possibly due to the blocking of the pores in the fiber by the acrylonitrile molecules.

### Dyeing Characteristics of the Grafted Polyester Fibers

**Disperse Dyes.** Generally, the dye uptake was found to increase with increasing amount of acrylic acid in polyester (Fig. 7). The dye uptake of polyester for Duranol Red 2R and Duranol Violet 2R were 4.025 and 2.08 g/kg of the substrate, respectively, while the corresponding values for 22.4% grafted polyester were 5.9 and 4.1 g/kg of the fiber. This increased uptake can be attributed mainly to the swelling of the fibers in the swelling medium.

**Basic and Direct Dyes.** Acrylic acid-grafted polyester fibers showed considerable uptake of basic dye (Fig. 8). The fibers containing 24.8% graft had a dye content for Astrazon Orange R and Astrazon Orange G of 22.0 and 24.5 g/kg of fibers, respectively. This can be attributed to the formation of salt linkages between acrylic acid and the basic dyes. Similar increase of dye uptake with increased grafting was also evident in the case

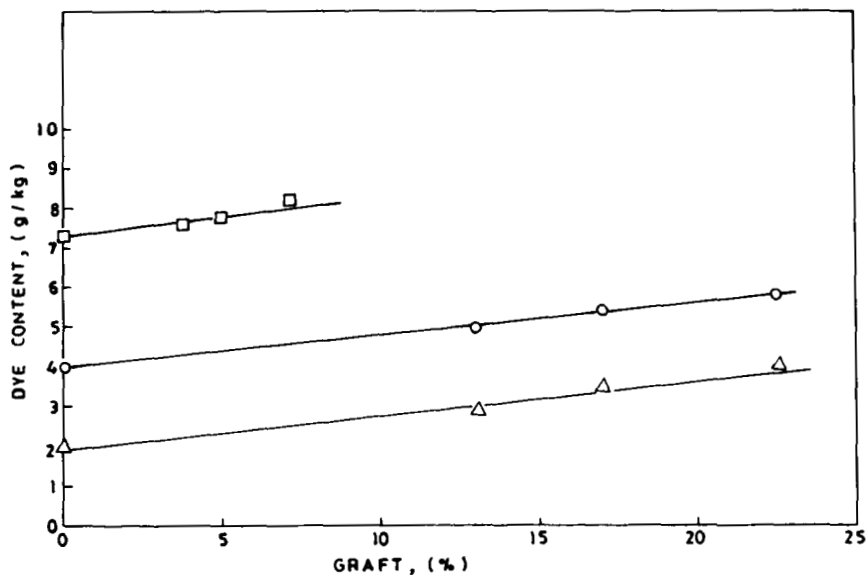


Fig. 7. Disperse dye content of AA-grafted PE: ( $\Delta$ ) Duranol Violet 2R, irradiation method; ( $\circ$ ) Duranol Red 2R, irradiation method, ( $\square$ ) Duranol Red 2R, benzoyl peroxide method.

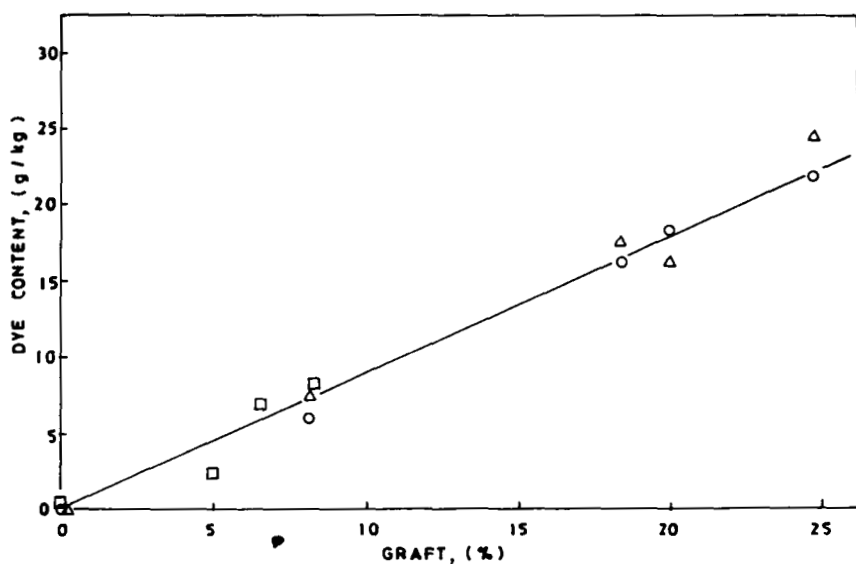


Fig. 8. Basic (cationic) dye content of AA-grafted PE fibers: ( $\circ$ ) Astrazon Orange R, irradiation method; ( $\square$ ) Astrazon Orange R, benzoyl peroxide method; ( $\Delta$ ) Astrazon Orange G, irradiation method.

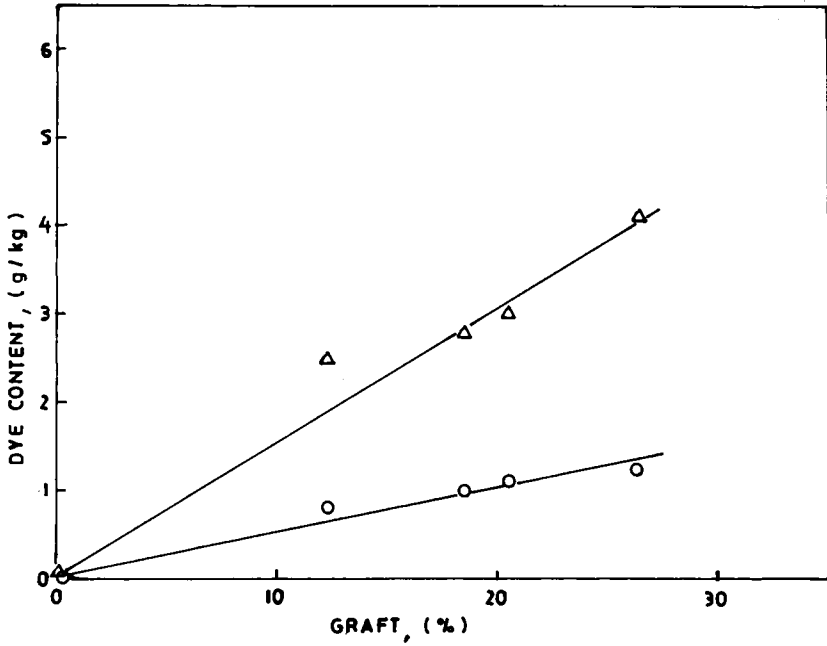


Fig. 9. Direct dye content of AA-grafted PE fibers: (Δ) Congo Red; (○) Chlorazol Sky Blue FF.

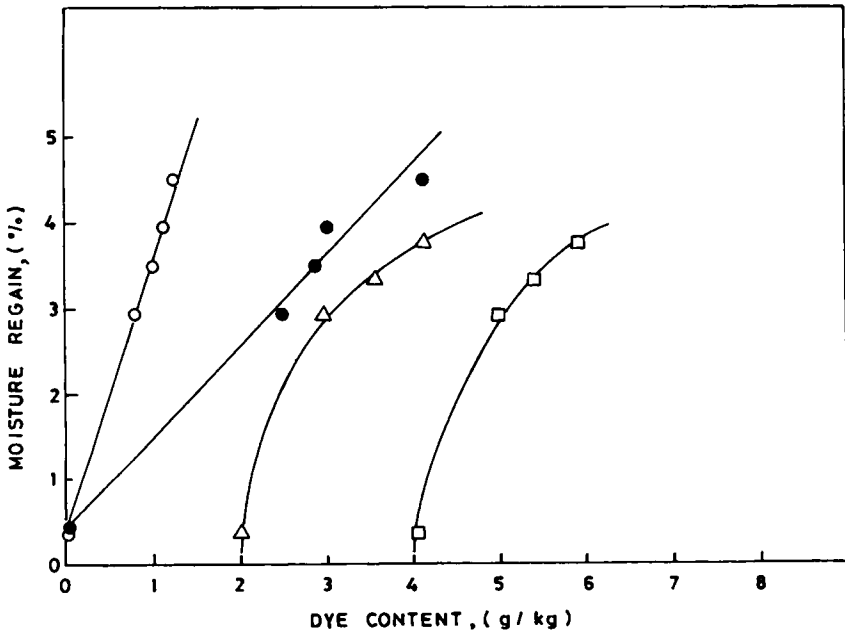


Fig. 10. Correlation between direct and disperse dye content and moisture regain of grafted PE fibers: (○) Chlorazol Sky Bue FF; (●) Congo Red; (Δ) Duranol Violet 2R; [□] Duranol Red 2R.

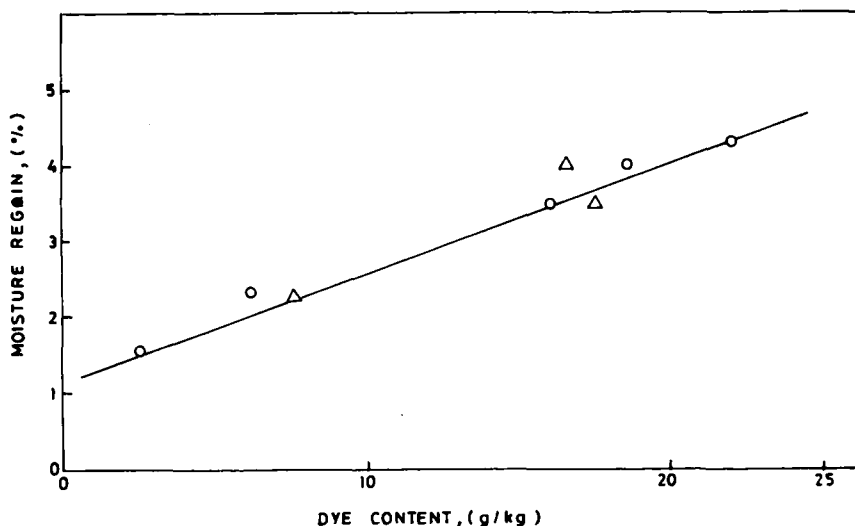


Fig. 11. Correlation between basic (cationic) dye content and moisture regain of grafted PE fibers: (O) Astrazon Orange R; (Δ) Astrazon Orange G.

of direct dyes (Fig. 9). Congo Red and Chlorazol Sky Blue FF, for example, showed a dye uptake of 4.14 and 1.25 g/kg for 26.4% grafted polyester fibers.

Another factor influencing the dye uptake for all the three classes of dyes is the increased hydrophilicity of the substrate as the number of acrylic acid units increases. This can be seen by correlating the moisture regain with dyeability, as shown in Figures 10 and 11. The best correlation is obtained for direct dyes, which give a linear relationship. In the case of basic and disperse dyes, although the relationship is not linear, there is still a correlation between the properties. The nonlinear behavior may be due to stretching of layers in the matrix of the polyester.

The dyeing characteristics of the chemically grafted fibers were almost identical with that of radiation-grafted material, as shown in Table II and Figure 8. This once again supports the earlier statement that the nature of the grafts in the two cases is not different.

When the dyeing of polyester fibers grafted with acrylonitrile was carried out with direct dyes, it was observed that even for the fibers containing the maximum amount of graft (40%), there was no direct dye absorption to any appreciable extent. This may be due to the fact that the acrylonitrile grafted on polyester does not increase the hydrophilicity of the grafted fibers, and hence there is no increase in the affinity of the fibers toward direct dyes. This is in accordance with the moisture regain values discussed earlier. The fibers grafted with acrylonitrile could be dyed with basic dyes, but beyond 17% graft there was only marginal increase in the dye uptake by the fibers. The quantitative estimations of the dye uptake were not possible as the dye could not be stripped off from the fiber quantitatively.



The polyester fibers containing nitrile groups in the graft copolymers were subjected to reducing treatment at about 60°C for 3 hr in a solution containing 1 *M* borohydride with a view to reduce the nitrile groups to amino groups. After the reduction, the samples were dyed with reactive dyes. The depth of the shade with reactive dyes depends upon the extent of grafting in the original fiber and the extent of reduction of the nitrile groups to amino groups. The amino groups thus obtained reacted with reactive dyes, and thus a fast dyeing with the conventional reactive dyes was possible.

### Electrokinetic Properties of Grafted and Ungrafted Polyester Fibers at Different pH Values of the Streaming Solution

**Zeta Potential.** Table III shows the relationship between zeta potential of polyester fibers and the pH of the streaming solution. When the pH of the streaming solution is increased from 3.5 to 10.9, there is a progressive increase in the negative values of the zeta potential up to a pH of 7.5. Thus, the negative value of the zeta potential increases from about -12 mV to -60 mV. With increase of pH beyond 7.5, the negative value of zeta potential decreased. On account of the hydrophobic nature of the polyester fibers, a strong negative potential is developed on the surface of the fiber when immersed in aqueous solutions. At very high alkaline pH and also extreme acidic pH values, some other additional factors influence the negative value of the zeta potential, such as the concentration of the sodium and chloride ions, respectively, and increased swelling inside the plug, especially under alkaline conditions, which account for the drop in those values.

Figures 12 and 13 show the effect of pH of the streaming solution on zeta potential of the grafted fibers. In general, the behavior of the grafted samples containing both acrylic acid and acrylonitrile graft is the same as in the case of pure polyester fibers, except that there is a little shift

TABLE III  
Electrokinetic Properties of PE Fibers at Different pH of Streaming Solution (HCl-NaOH)<sup>a</sup>

pH	Conductivity of solution, $\times 10^{-4}$ ohm <sup>-1</sup>	Resistance of solution, $\times 10^{+4}$ ohm	Conductivity of plug, $\times 10^{-4}$ ohm <sup>-1</sup>	Resistance of plug, $\times 10^{+4}$ ohm	Zeta potential, -mV	Surface charge density, e.s.u./cm <sup>2</sup>
3.5	3.0	0.325	1.9	0.48	12.27	135.8
4.7	0.17	5.3	0.12	7.9	29.25	90.38
5.5	0.086	13.0	0.0425	22.0	43.86	55.05
6.05	0.054	18.0	0.033	31.0	55.29	43.54
7.25	0.18	5.2	0.098	8.0	59.67	21.80
8.6	0.49	1.9	0.31	3.0	57.77	92.47
10.9	1.4	0.66	0.98	0.9	51.75	630.00

<sup>a</sup> Cell constant 1.388.

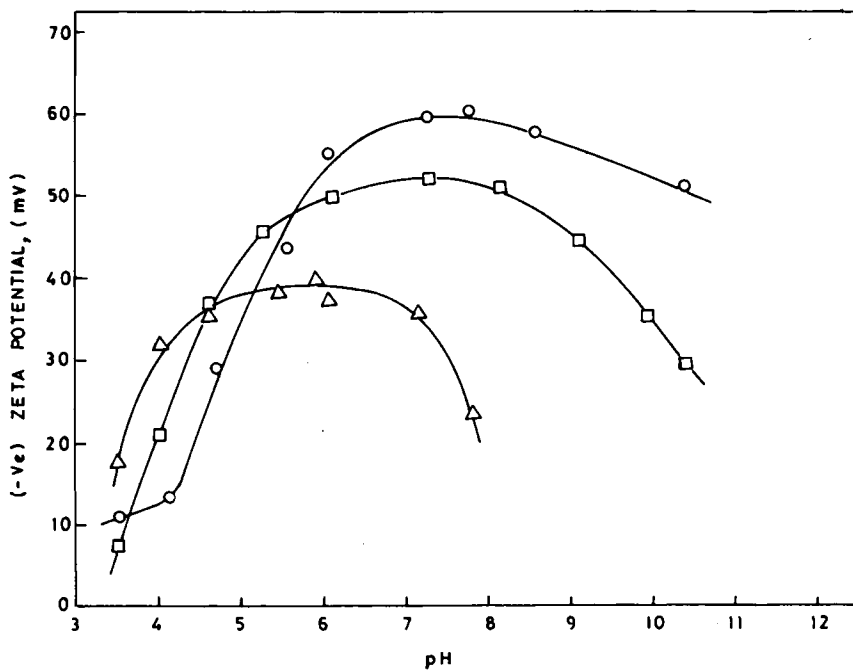


Fig. 12. Zeta potential of acrylic acid-grafted PE fibers vs. pH: (O) control; ( $\square$ ) 3.7% graft; ( $\Delta$ ) 18.4% graft.

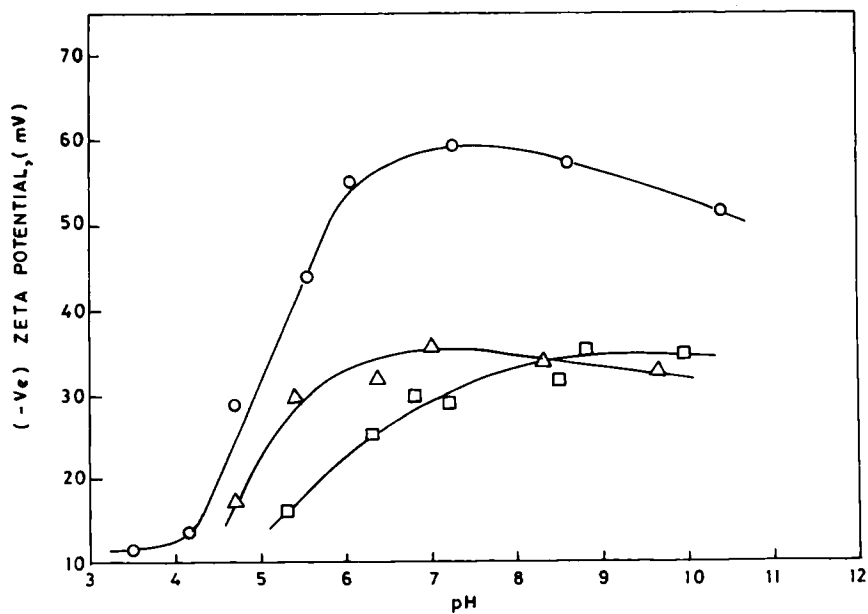


Fig. 13. Zeta potential of acrylonitrile-grafted PE fibers vs. pH: (O) control; ( $\Delta$ ) 8% graft; ( $\square$ ) 20.5% graft.



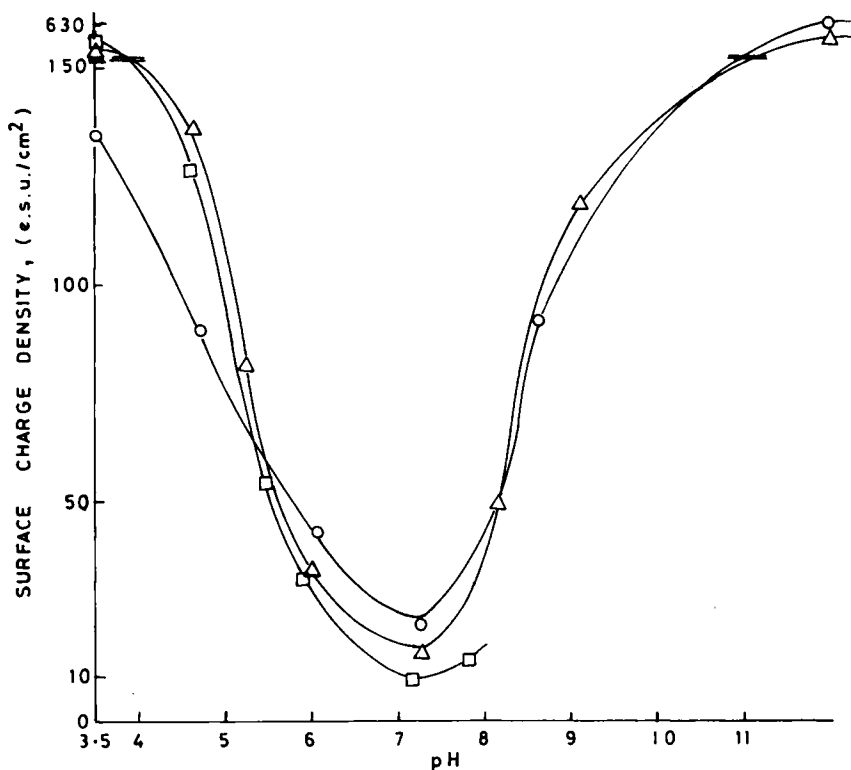


Fig. 14. Surface charge density of acrylic acid-grafted PE fibers: (O) control; ( $\Delta$ ) 3.7% graft; ( $\square$ ) 18.4% graft.

in the maximum obtained in the curve of zeta potential against pH. With the increased amount of acrylic acid graft, more and more of the alkaline solution is used for the satisfaction of the carboxylic groups in the fiber, and the maxima shift toward lower pH. The nitrile groups are less polar than the carboxyl groups and are therefore less susceptible to the change in pH as far as the maxima in the curve of zeta potential against pH are concerned.

**Surface Charge Density (S.C.D.).** Figures 14 and 15 show the results of surface charge density (S.C.D.) of polyester fibers grafted with acrylic acid and acrylonitrile. It can be seen that the value of S.C.D. is minimal at about pH 7 for all the fibers containing varying amount of the graft of acrylic acid and acrylonitrile. This minimum value of S.C.D. decreased with increase in the amount of graft in the fiber substrate. In case of acrylonitrile, there is hardly any change with increase in grafting. With increasing amount of graft in the fiber, it seems that the effective surface area of the fiber is reduced, and therefore a decrease in S.C.D. values was observed when a solution of pH 7 was streamed through. In acidic and alkaline media, various kinds of ions are present on the surface and in its vicinity, and hence the S.C.D. increased sharply in both these media.

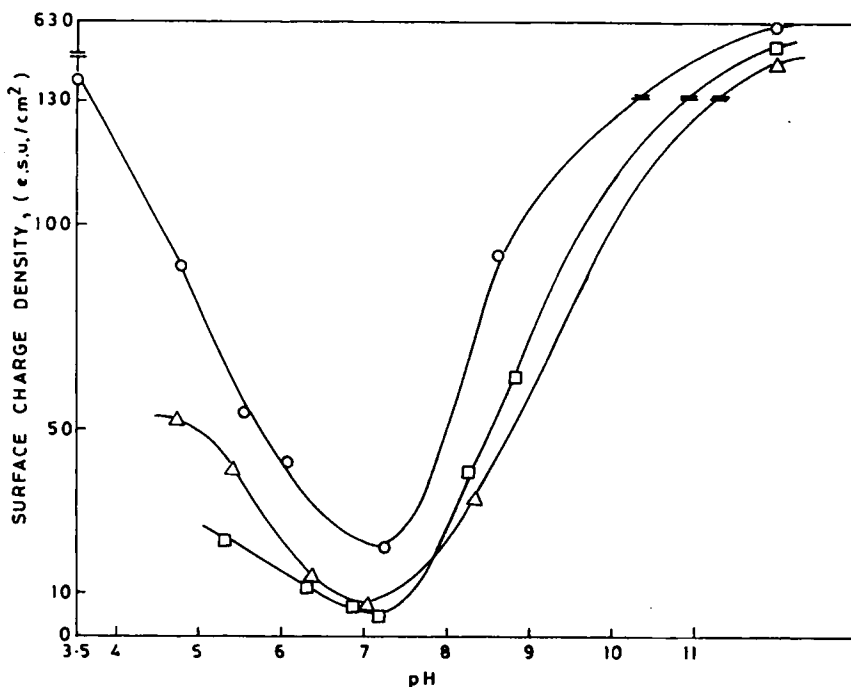


Fig. 15. Surface charge density of acrylonitrile-grafted PE fibers: (O) control; ( $\Delta$ ) 8% graft; ( $\square$ ) 20% graft.

**Surface Conductivity.** Specific conductivity of streaming solution ( $K_s$ ) and of the plug ( $K_p$ ) was also determined. Surface conductivity of the fibers ( $K_f$ ) was obtained by taking the difference between  $K_s$  and  $K_p$ . Surface conductivity of the fiber will be high if more functional groups are situated on the surface. The surface conductivity will be reduced, on the other hand, if either the total surface area of the fiber is reduced or the total number of functional groups on the surface is ineffective in character.

The surface conductivity of the polyester fibers grafted with acrylic acid and acrylonitrile was determined at different pH values for varying amounts of grafts in the fiber material. The results are shown in Figures 16 and 17. The surface conductivity of AA-grafted fibers was considerably higher in alkaline pH than in neutral or acidic medium. In the case of acrylonitrile, at low values of percentage graft, there was only marginal increase in the surface conductivity in the alkaline range. At higher values of acrylonitrile (20.5%), the surface conductivity of the fibers progressively decreased with increase in pH. Moreover, both the plots are straight lines unlike those in the case of acrylic acid grafts. This shows that the surface conductivity is not very much influenced by either the acidic or alkaline nature of the streaming solution. In the case of acrylonitrile grafts, it appears that the reduction in the effective surface area plays a more important role than the contribution by the nitrile groups toward surface conductivity (Fig. 17).

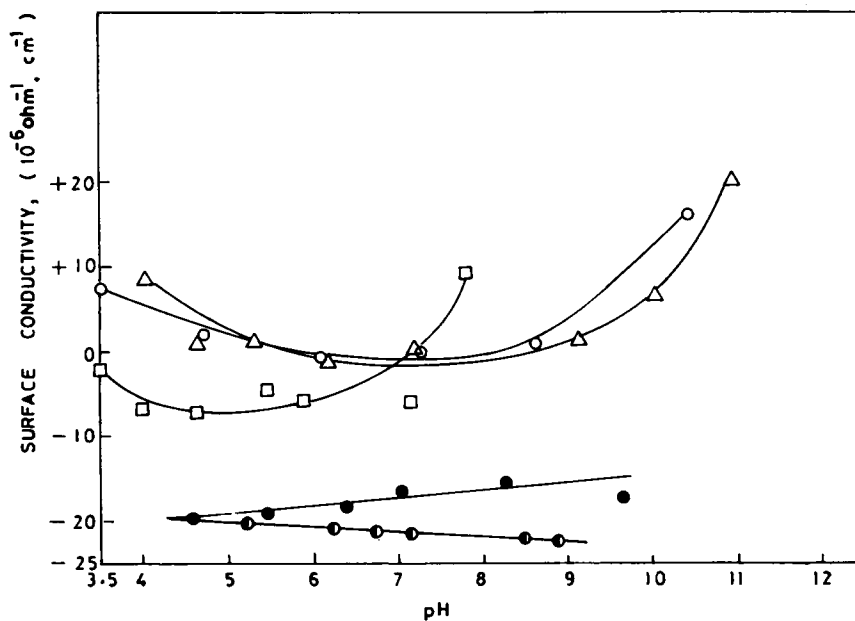


Fig. 16. Surface conductivity of grafted PE fibers: (○) control; (△) 3.7% acrylic acid graft; (□) 18.4% acrylic acid graft; (●) 8% acrylonitrile graft; (●) 20% acrylonitrile graft.

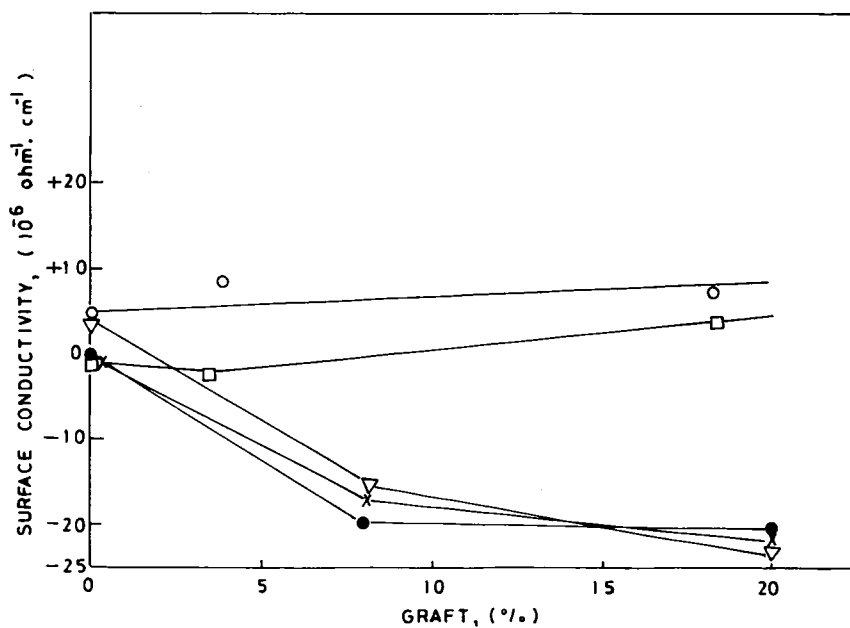


Fig. 17. Surface conductivity vs. graft on PE fibers: (○) pH 4, acrylic acid graft; (□) pH 7, acrylic acid graft; (●) pH 5.5, acrylonitrile graft; (×) pH 7, acrylonitrile graft; (▽) pH 9, acrylonitrile graft.

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