Grafting Onto Polyester Fibers. III. Electrokinetic Properties of Acrylic Acid and Acrylonitrile-Grafted Polyester Fibers In the Presence of Cationic Dyes

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Synopsis

The electrokinetic properties such as zeta potential, surface charge density, and surface conductivity of polyester fibers grafted with acrylic acid and acrylonitrile were measured when cationic dye solutions were streamed through. The presence of the cationic dyes on the surface of the fibers and their specific adsorption at the carboxylic groups in the acrylic acid graft copolymer produce lowering of zeta potential. The decrease in surface charge density as the percent graft increases is due to the decrease in surface area of the fibers due to the adsorption of the cationic dyes. The same trend is observed with acrylonitrile-grafted fibers. The surface conductivity of the acrylonitrile-grafted polyester fibers increases with increase in dye concentration of the streaming solution. The results for the 27.4% grafted sample differed from those of the 7.32% and 12.1% grafts, which is indicative of the formation of a three-dimensional network causing change in both the physical structure as well as the chemical nature of the surface of the substrate.

INTRODUCTION

All hydrophobic synthetic fibers including polyester fibers possess high negative zeta potential. When polyester is modified through grafting, various functional groups are introduced into the fiber macromolecules, and hence the zeta potential of such fibers will be influenced to a great extent. It will be further influenced by various dye solutions, since the dye cations or anions will have interaction with the functional groups present in the grafted polyester fibers. Such a study is important from the point of view of knowing the extent of introduction of the functional groups as well as the nature of the interaction between these groups and dye ions so that the dyeing mechanism and the influence of grafting on the dyeability of polyester fibers with various classes of dye could be understood.

In an earlier communication[1] the effect of grafting acrylic acid and acrylonitrile on polyester fibers on their electrokinetic properties was reported. In general, as the amount of these components increased, there was a decrease in the (negative) value of the zeta potential at a given pH, which was attributed to increase in the hydrophilicity of the fibers as a result of grafting. Lowering of surface charge density and surface area of fibers as a result of grafting were also observed.

Suzawa and Yuzawa[2] determined the zeta potential and surface charge density of polyester fibers in the presence of surfactants adsorbed per unit area of the fiber and observed that this amount was directly proportional to the concentration of surfactants in streaming solution.

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Jacobasch and co-workers[3,4] reported that polyester fibers with a large maximum zeta potential possess strong inclination for the adsorption of particles of dry pigment. Kanamaru[5] observed a fall in zeta potential of polyester fibers with progressive increase in absorption of water vapor. The literature survey, however, shows that very limited work has been reported describing the changes in the electrokinetic properties of polyester fibers as a result of adsorption of dye molecules from streaming solution.

The present paper describes the variation in zeta potential, surface charge density, and surface conductivity of polyester fibers before and after graft copolymerization with acrylic acid and acrylonitrile in the presence of varying concentrations of cationic dyes in streaming solution.

EXPERIMENTAL

Materials

Terene polyester fiber (1.5 D × 1.5 in. KK_2A) manufactured by Chemicals and Fibres of India (CAFI), Bombay, was used. This fiber along with the grafted polyester fiber was used to determine the zeta potential.

The following purified dyes were used in the present investigation: (i) Sandocryl Blue B3G (C.I. Basic Blue 3); (ii) Sandocryl Red B6B (C.I. Basic Violet 16); (iii) Sandocryl Orange BG (C.I. Basic Orange 21).

TABLE I
Changes in Electrokinetic Properties of Acrylic Acid-Grafted PE Fibers in the Presence of Cationic Dyes

Concentration, 10^{-5} M	ζ, −mV 3%[a]	ζ, −mV 18%[a]	σ, esu/cm^2 3%	σ, esu/cm^2 18%
		C.I. Basic Violet 16		
—	45.6	29.5	13.6	6.45
2.0	32.5	—	101.3	—
2.5	24.4	—	75.5	—
3.0	17.3	12.15	63.8	45.2
4.0	14.2	9.20	60.2	39.00
5.0	—	8.22	—	38.10
6.0	10.07	7.36	54.2	38.00
8.0	—	7.22	—	42.51
10.0	—	4.85	—	31.8
		C.I. Basic Blue 3		
—	45.6	29.5	13.6	6.45
2.0	6.65	—	19.75	—
2.5	3.36	—	11.14	—
3.0	3.28	—	11.83	—
3.5	3.15	—	12.38	—
5.0	—	6.21	—	28.24
5.55	—	4.73	—	23.32
7.55	—	2.21	—	12.80
8.55	—	1.61	—	11.35

[a] Percent graft.

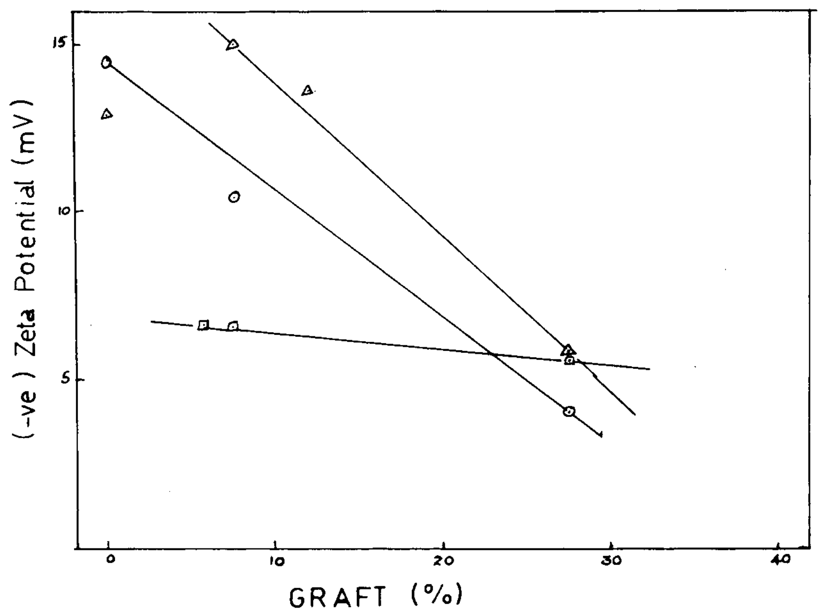

Fig. 1. Zeta potential of acrylonitrile-grafted polyester fibers vs. graft %: (O) C.I. Basic Violet 16; (▲) C.I. Basic Blue 3; (◆) C.I. Basic Orange 21 (1×10^{-5} g-mole/l. of dye).

Purification of Dyes

Purification of cationic dyes was carried out according to the method suggested by Balmforth et al.[6] The dye was extracted with 10 volumes boiling absolute alcohol. Easily filterable crystals were recovered after chilling the solution overnight. This procedure was repeated thrice to ensure good purity (99.9%).

Determination of Electrokinetic Properties

Determination of streaming potential, calculation of zeta potential, surface charge density, and surface conductivity has been discussed in a previous communication.[1] The pH of the dye solution was 7. Reproducibility of the measurements was fairly good.

RESULTS AND DISCUSSION

In the previous communication on the effect of grafting of acrylic acid and acrylonitrile onto polyester on their electrokinetic properties, it was reported that, in general, the (negative) value of the zeta potential at a given pH decreased with a progressive increase in graft content on the polyester fibers.[1] This was attributed to increased hydrophilicity of the polyester fibers as a result of grafting. The surface charge density of the grafted polyester fibers showed a good correlation, giving a linear relationship between the two parameters. Studies on surface conductivity revealed that nitrile groups were less susceptible toward change in pH of the streaming solution than the carboxyl groups of the graft copolymer. It was observed that the reduction in the effective surface area of the fiber as a result of grafting played a more important role than the contribution by nitrile groups toward surface conductivity.

Table I shows the effect of changes in cationic dye concentration in the streaming solution on the electrokinetic properties of acrylic acid-grafted polyester fiber. In general, with increase in the amount of dye in the streaming solution, there is a progressive decrease in the (negative) value of the zeta potential of the acrylic acid-grafted polyester fibers. Such a decrease is also in-

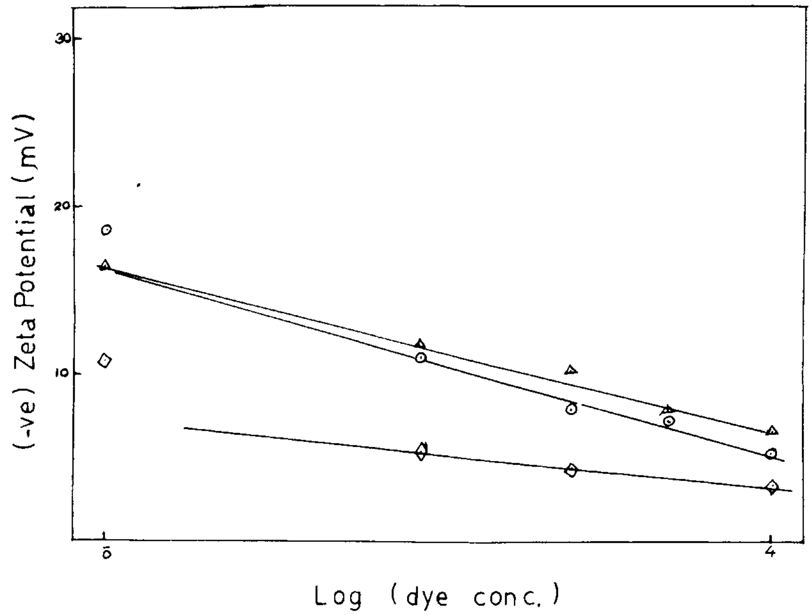

Fig. 2. Zeta potential of acrylonitrile-grafted polyester vs. dye concentration at 7.32% graft: (O) C.I. Basic Violet 16; (▵) C.I. Basic Blue 3; (◇) C.I. Basic Orange 21.

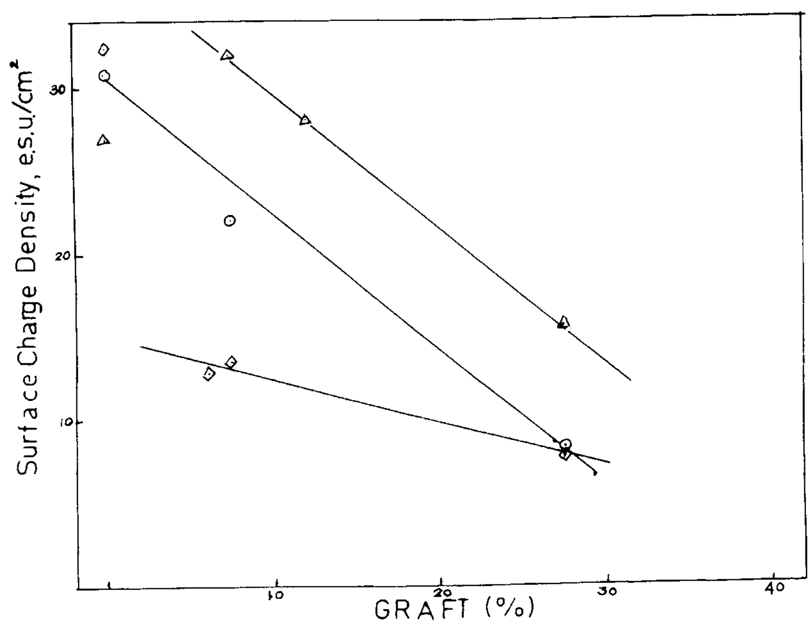

Fig. 3. Surface charge density of acrylonitrile-grafted polyester vs. graft %: (O) C.I. Basic Violet 16; (▵) C.I. Basic Blue 3; (◇) C.I. Basic Orange 21.

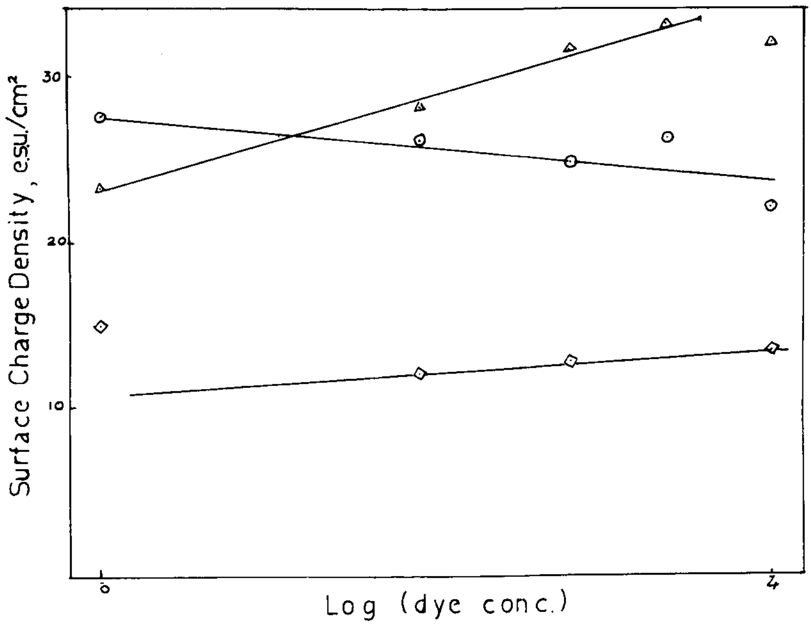

Fig. 4. Surface charge density of acrylonitrile-grafted polyester vs. dye concentration at 7.32% graft: (○) C.I. Basic Violet 16; (△) C.I. Basic Blue 3; (◇) C.I. Basic Orange 21.

fluenced by the amount of acrylic acid copolymer in the polyester fibers; the higher the amount of acrylic acid copolymer in the polyester fibers, the faster is the decrease in the zeta potential. Thus, the zeta potential is decreased from −45.6 to −10.07 mV in case of acrylic acid-grafted (3%) polyester fibers when the concentration of C.I. Basic Violet 16 in the streaming solution was changed from zero to 6×10^{-5} *M*. The corresponding values of the zeta potential varied from −29.5 to −4.85 mV when the dye concentration was changed from zero to 1×10^{-4} *M* in case of 18% acrylic acid graft. It is likely that the presence of dye cations on the surface of the fibers and their surface absorption at the carboxyl groups in the graft copolymer bring about lowering of the zeta potential of the fibers.

It is therefore obvious that for higher amounts of acrylic acid graft there is increased reduction in the (negative) value of the zeta potential as a result of an increased number of carboxyl groups in the grafted fibers. The trend has been reflected in both dyes, i.e., C.I. Basic Violet 16 and C.I. Basic Blue 3, although the absolute values of the zeta potential at equivalent concentrations of the dyes in the streaming solution differ to certain extent, which may possibly be attributed to the difference in the chemical constitution of these two dyes.

Surface Charge Density

In general, the surface charge density (S.C.D.) is lowered as a result of increased amounts of dye in the streaming solution. Thus, for fibers of 3% acrylic acid graft, the S.C.D. was decreased from 101.3 esu/cm^2 to 54.2 esu/cm^2 when the dye concentration was increased from 2×10^{-5} *M* to $6 \times 10^{-5}M$. For 18% graft, the corresponding values of the S.C.D. were 45.2 and 31.8 esu/cm^2, respectively, when the dye concentration varied from $3 \times 10^{-5}M$ to $1 \times 10^{-4}M$. For any given

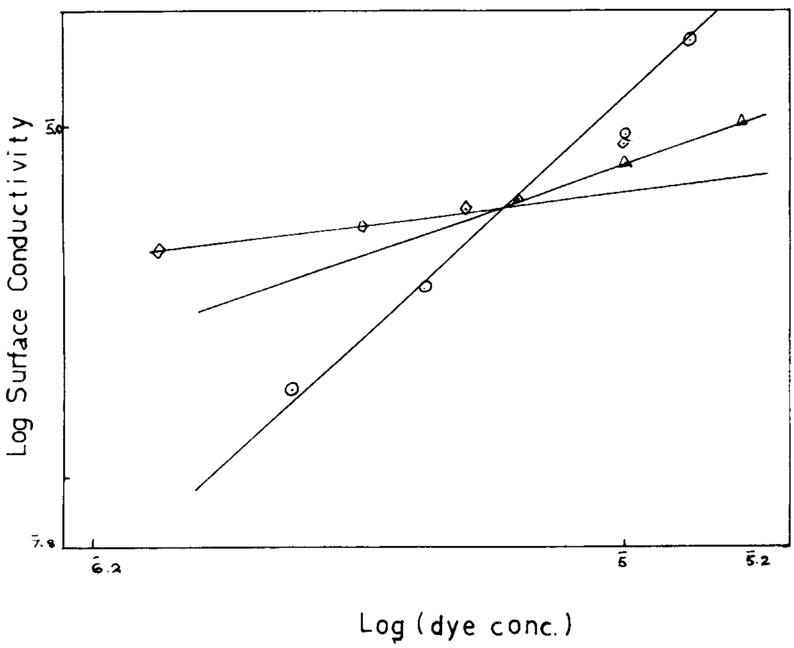

Fig. 5. Relation between surface conductivity of acrylonitrile-grafted polyester and dye concentration (C.I. Basic Violet 21): (O) 7.32%; (▲) 12.0%; (◊) 27.4%.

concentration of the dye, the absolute value of S.C.D. was lower in case of higher amounts of graft. Thus, when the streaming solution contained $4 \times 10^{-5}M$ C.I. Basic Violet 16, the values of the S.C.D. for 3% and 18% graft contents were 60.2 and 39.0 esu/cm^2, respectively. A similar trend was observed in case of C.I. Basic Blue 3.

The extent of lowering the S.C.D. for both, i.e., 3% and 18% grafts, was different for different dyes studied. This is possibly due to the difference in the chemical constitution of the dyes streamed, viz., C.I. Basic Violet 16 and C.I. Basic Blue 3. This difference in chemical structure of the dyes is reflected in differential absorption of dye cations which leads finally to the decrease in the surface area of the fibers.

Acrylonitrile-Grafted Polyester Fibers

The zeta potential, surface charge density, and surface conductivity of acrylonitrile-grafted polyester fibers were determined in the presence of varying concentrations of the three cationic dyes in streaming solution, i.e., C.I. Basic Violet 16, C.I. Basic Blue 3, and C.I. Basic Orange 21.

Typical results for one concentration ($1 \times 10^{-5}M$) have been plotted in Figure 1. The figure gives change in (negative) value of the zeta potential with respect to acrylonitrile graft in the presence of the three dyes. In general, the negative value of zeta potential decreased with increase in graft content when a solution of given concentration was streamed through. Figure 2 gives the plot of negative value of zeta potential of acrylonitrile-grafted polyester and log dye concentration. A good correlation can be seen for all the three dyes studied. The negative value of the zeta potential decreased progressively with increase in the dye

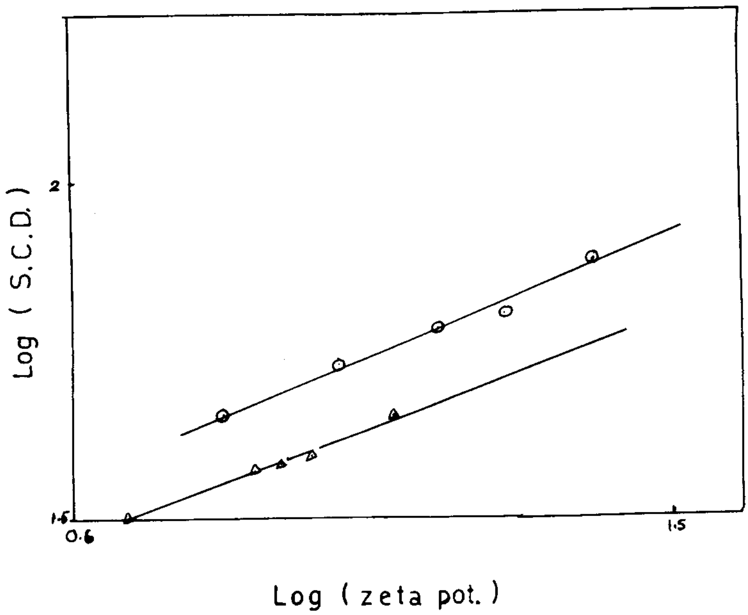

Fig. 6. Correlation between zeta potential and surface charge density of acrylic acid-grafted polyester at different concentrations of cationic dye (C.I. Basic Violet 16): (○) 3%; (▲) 18%.

concentration in the streaming solution. This may be attributed to the neutralization of negative charge as a result of increase in absorption of dye cations at the —CN groups in the grafted polyester fiber. The absolute values of the zeta potential for a given amount of graft at a given dye concentration vary to a certain extent among the three cationic dyes studied. This may be due to the difference in the chemical constitution of these dyes.

Surface Charge Density

Figures 3 and 4 give results on S.C.D. of acrylonitrile-grafted polyester fiber in the presence of the three cationic dyes. Figure 3 is a plot of S.C.D. versus amount of acrylonitrile graft in the presence of the cationic dyes. In general, as the graft amount increases, there is a linear decrease in S.C.D., possibly due to the increased absorption of the dye by the grafted sample, thus decreasing the surface area.

Figure 4 shows a linear correlation between S.C.D. and log dye concentration for acrylonitrile-grafted polyester (7.32%). No definite trend is however observed as regards either increase or decrease in S.C.D. The increased absorption of dye may bring about an increase in S.C.D. but at the same time a substantial decrease in effective surface area of the fiber as a result of the presence of graft copolymer chains as well as the layer of the dye cations. Moreover, some other factors may be contributing to this situation, such as change in physical state and chemical nature of polyester fiber possibly forming a three-dimensional network in the fiber structure through graft copolymer chains. Such a network may bring about not only a reduction in total surface area of the fiber but also hindrance to flow and absorption of dye cation.

Surface Conductivity

Figure 5 gives the results of surface conductivity of acrylonitrile-grafted polyester sample in the presence of varying concentrations of a cationic dye in the streaming solution. A linear relationship exists between surface conductivity and dye concentration in streaming solution on a log–log scale. The slopes of the straight lines representing fibers containing lower amounts of graft, i.e., 7.32% and 12.1%, are almost identical. However, the 27.4% grafted sample was distinct from others in its surface conductivity. This is probably due to the different physical structure of the fiber containing high amounts of graft. In general, the surface conductivity of the grafted polyester fiber increases with increase in dye concentration in the streaming solution for all three dyes studied.

Figure 6 gives a log–log correlation between zeta potential and surface charge density in the presence of a cationic dye with respect to acrylic acid-grafted fibers. An excellent correlation is observed which however was not seen in the case of acrylonitrile grafted polyester fiber in presence of the same cationic dye. These results seem to indicate that the absorption of dye cation is more quantitative with respect to functional groups such as —COOH in case of acrylic acid-grafted polyester fibers than —CN in acrylonitrile-grafted polyester fibers. The apparent maxima observed in Figures 1 and 3 in case of the dye C.I. Basic Blue 3 may be neglected since the different chemical structure of this dye and the absence of very high reproducibility of the measurements may be responsible for such a behavior.

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