

Electrokinetic Properties of Modified Polyester Fibers

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SYNOPSIS

Electrokinetic properties of normal polyester flat filament, texturized polyester and cationic dyeable polyester were studied when solutions of different pH and cationic dye concentrations were run through them. The textured polyester exhibited maximum negative zeta potential whereas cationic dyeable polyester showed minimum. The negative zeta potential was found to be maximum near neutral pH. The effect of heat-setting at extreme conditions (220°C, 90 s) on electrokinetic properties was also studied. Such heat-setting was found to lower negative zeta potential, attributed to a decrease in surface area. Cationic dyeable, "easy" dyeable, and normal flat filament type polyester were also investigated. Results with respect to negative zeta potential, surface charge density, and surface conductivity, are discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

All hydrophobic synthetic fibers including polyester possess high negative zeta potential. When polyester is modified through grafting of vinyl monomers, various functional groups are introduced into the fiber macromolecules. The zeta potential of such fiber is influenced to a great extent, when solutions of different dye concentrations or H-ion concentrations are streamed through, because the dye ions or H-ions have interaction with these functional groups.¹⁻⁴

Jacobasch and Flath⁵ have shown that thermal treatment of wet drawn polyamide (nylon-6) filament shifted the maximum zeta potential to a higher concentration of electrolyte (sodium chloride), simultaneously reducing its absolute values. It was reported that the changes in the zeta potential were caused by changes in the fine structure of filaments.

The use of texturized polyester yarn as well as cationic dyeable (CDPET) and easy dyeable polyester (EDPET) is increasing day-by-day because of the added advantages of these fibers over normal flat filament yarns. Texturing improves comfort, wrinkle resistance, drapability, and resiliency. Cat-

ionic dyeable polyester is manufactured by introducing compounds containing the sulfonic acid group, that is, sodium salt of 5-sulfoisophthalic acid, during the polymerization stage. This fiber can be dyed with cationic dyes and it produces attractive fancy shades. As far as EDPET is concerned, there are number of ways to obtain the easy dyeability or in other words dyeability with disperse dye at boiling temperature without the use of carriers. These fibers are also known as carrier-free dyeable polyester. The glass-transition temperature of such a fiber is slightly reduced by incorporating aliphatic glycols of higher chain length during the polymerization stage in addition to the normal materials.

A literature survey clearly indicates that no work has been reported on the electrokinetic properties of polyester fibers modified thermally, that is, texturized polyester or those manufactured by incorporating different comonomers at the polymerization stage, that is, cationic dyeable or easy dyeable polyester. Hence the present paper describes the variation in electrokinetic properties of different heat-set and unset polyester fibers, when solutions of different pH or cationic dye concentrations were streamed through.

The present paper is subdivided into two different sets, because each set deals with a triplet of fibers slightly different in specifications of fineness, heat-setting conditions, etc.

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EXPERIMENTAL

Materials

Fibers

The following commercially available polyester filament yarns were used after removing oligomers and spin oil by extraction with ether in a soxhlet extractor and then scouring at 70°C for 30 min using 2 g/L nonionic detergent.

1. normal polyester (NPET) [50^D/36] and [76^D/36], flat filaments,
2. textured normal polyester (Tex-NPET) [85^D/34],
3. easy dyeable polyester (EDPET) [50^D/40],
4. cationic dyeable polyester (CDPET) [50^D/24] and [76^D/36].

NPET, EDPET, and CDPET were obtained from Nirlon Synthetic Fibers and Chemicals Ltd., Bombay, India. Tex-NPET was obtained using partially oriented yarn of normal polyester type from Nirlon Synthetic Fibers and Chemicals Ltd., and subsequently texturized in Beekaylon Industries Pvt. Ltd., Bombay, India.

Dye

Sandocryl Blue B-3G (C. I. Basic Blue 3), supplied by Sandoz Ltd. (India), was used after purification.

Heat-Setting

In order to get maximum changes in internal structure of the fiber, the yarn samples were heat-set at 220°C for 90 s in a hot air chamber in relaxed condition. These samples were used in the first set of experiments.

The second set deals with the fiber samples in yarn form, heat-set at 180°C for 90 s in relaxed condition.

Determination of Electrokinetic Properties

Determination of streaming potential and calculations of zeta potential, surface charge density, and surface conductivity have been described in the literature.^{1,6} The pH of streaming solution of varying cationic dye concentrations, was maintained at 5, because cationic dyeing is done at this pH.

Estimation of Fineness of Yarn

Determination of Nominal Linear Density Values of Yarn. This was done using a Vibroscope per the standard method described in the literature.⁷

Determination of Yarn Denier. A direct method of weighing a definite length of unset and heat-set yarn on an electronic balance was followed to estimate the yarn denier.

Micronaire Value. The micronaire values of yarn samples were determined by using a Sheffield Micronaire instrument per the standard method.⁸

RESULTS AND DISCUSSION

Set I

This set involves three fibers: flat filament of normal and cationic dyeable polyester and both 76^D/36 and textured normal polyester of 85^D/34.

Set Ia: Effect of pH of Streaming Solution on Electrokinetic Properties

At the outset, the solutions of different pH were streamed through plugs of NPET, CDPET, and Tex-NPET samples. The electrokinetic properties such as zeta potential, surface charge density, and surface conductivity were quantitatively determined. These results are given in Figures 1–3 for negative zeta potential, surface charge density, and surface conductivity, respectively. It is clear from Figure 1 that

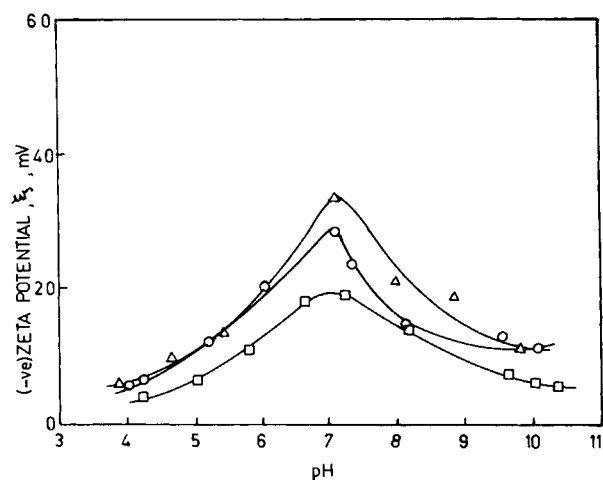


Figure 1 Relation between zeta potential and pH of the streaming solution: (O) NPET; (Δ) Tex-NPET; (\square) CDPET.

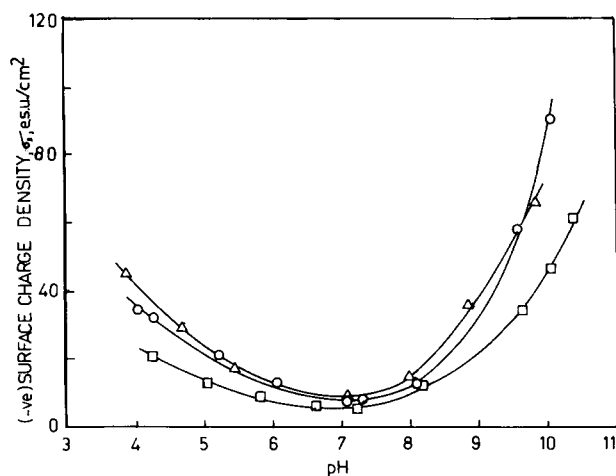


Figure 2 Relation between surface charge density and pH of the streaming solution: (○) NPET; (△) Tex-NPET; (□) CDPET.

the negative zeta potential of all the polyester samples was at a maximum around neutral pH and was found to increase as pH of the streaming solution was varied from 4 to 7. This increase in negative zeta potential with increase in pH is attributed to the continuous increase in the extent of dissociation of carboxylic groups. On the alkaline side, however, continuous decrease in negative zeta potential seemed to be favored, which may be attributed to the surplus concentration of alkali in relation to carboxyl content of the fiber and to the dominating influence of positively charged sodium ions in the streaming solution over the hydroxyl groups. At the very high concentration of alkali, changes in the electrical double layer may be taking place due to the adsorption of sodium cations, drastically reducing the negative zeta potential.¹ As far as the maximum values of negative zeta potential of the fibers were concerned, it was found to be highest in the case of Tex-NPET and least in the case of CDPET.

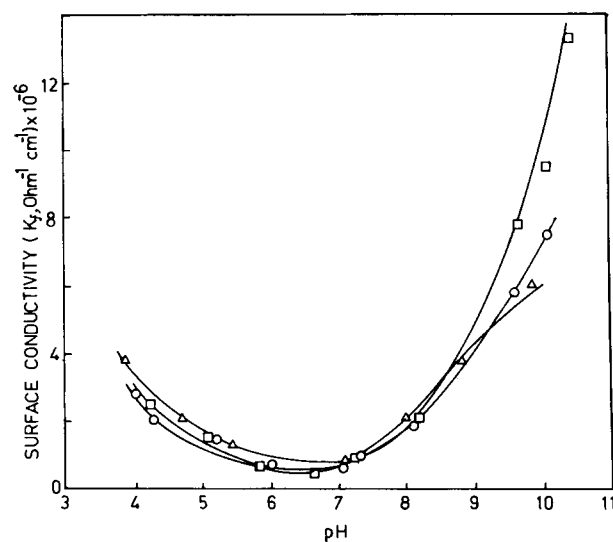


Figure 3 Relation between surface conductivity and pH of the streaming solution: (○) NPET; (△) Tex-NPET; (□) CDPET.

These results indicate that texturing of polyester increased the negative zeta potential, which may be attributed to an increase in the specific surface area of the fiber during texturing.

It is well known that the bulk of the fiber during texturing increases, resulting in an increase in the specific surface area. The data in Table I clearly indicates that the denier per filament of the flat filament NPET was lower than that of Tex-NPET which leads to the conclusion that the specific surface area of the Tex-NPET should be less than that of flat filament. This was the inference from the observations made not only with the yarn denier measured, but also with the nominal linear density measured on the Vibroscope. However, such an inference is valid only if the denier is changed in the same category of the substrate. The fact that the flat filament NPET and the Tex-NPET have dif-

Table I Fineness and Specific Surface Area of Different Polyester Fibers

Sample	Filament Denier	Nominal Linear Density (by Vibroscope)	Micronaire Values	Specific Surface Area
Flat filament NPET	2.11	2.15 (2.56)	5.85	0.413K ^a
Tex-NPET	2.50	2.97 (3.07)	5.75	0.417K
Flat filament CDPET	2.11	2.20 (2.65)	6.05	0.406K

Values in parentheses are to heat-set sample.

^a K, constant.

ferent thermal deformation history, makes measurement of surface area by an independent method essential. The microunits values⁸ were determined and indicated that a lower microunits value was observed for Tex-NPET than that of flat NPET. Consequently, the higher specific surface area of Tex-NPET could be due to the effect of the texturization process itself, which is known to increase the bulk of the fibers. As far as the flat filament CDPET was concerned, although the filament denier was equivalent to that of NPET, its microunits values were found to be highest and hence the specific surface area was found to be the least. This low specific surface area, assisted by the higher polarity due to sodium salt of 5-sulfoisophthalic acid unit in its polymeric chain, were responsible for the low negative zeta potential exhibited by CDPET.

Figures 2 and 3 show the effect of the pH of the streaming solution on the surface charge density and surface conductivity of different polyester fibers. In general, all the fibers gave minimum surface charge density and surface conductivity value at and around neutral pH. The critical pH corresponding to a minimum in these values remained almost unaltered in the range of 7 ± 0.2 for the different polyester fiber samples. The minimum surface charge density at critical pH may be attributed to the least ionic concentration that subsequently increased on either side of this critical pH because of the progressive increase in ionic concentration at and around the fiber surface and fiber-liquid interphase. The CDPET exhibiting the least negative zeta potential also had the lowest surface charge density among the three fibers.

At a particular pH, with the ionic interaction of the functional groups on the surface of the fiber and

the ions in the streaming solution being minimum, the surface conductivity was found to be the lowest. However, as the pH was varied up or down, the surface conductivity of the fibers increased due to the increase in the ionic interaction between the ions on the fiber surface and in the fiber-liquid interphase. It is also clear that, surface conductivity of the fibers increased more on the alkaline side than on the acidic side. This may be caused by the presence of carboxyl groups in polyester. Such behavior was further enhanced when anionically modified polyester (CDPET) was used. Hence, in the case of CDPET at the highest pH, surface conductivity was tremendously enhanced.

Set Ib: Effect of Cationic Dye Concentration in Streaming Solution on Electrokinetic Properties

The solutions containing various concentrations of cationic dye (Sandocryl Blue B-3G at pH 5) were streamed through the plugs of different polyester fiber samples in unset as well as in the heat-set (220°C, 90 s) form and electrokinetic properties were accordingly determined. The selection of this heat-setting temperature and time was based on the fact that this heat-setting condition brought about considerable variation in the internal structure of the fiber, due to the occurrence of secondary crystallization. Numerous small crystals melted and fused to form big crystals and then a small number of big crystals are created, giving higher free volume per crystal responsible for a considerable increase in disperse dye uptake of polyester when heat-set under these conditions.

Data in Table II indicates that with an increase in the amount of cationic dye in the streaming so-

Table II Effect of Dye Concentration in Streaming Solution on Negative Zeta Potential of Different Polyester Fibers

Concentration of Dye Solution at pH 5 ($M \times 10^{-6}$)	(-ve) Zeta Potential (mV)					
	Flat Filament NPET		Text-NPET		CDPET	
	Unset	Set	Unset	Set	Unset	Set
10	9.91	9.38	11.57	10.04	8.92	8.12
20	9.16	8.70	9.55	8.20	8.25	7.08
40	7.93	7.52	7.54	6.72	6.45	5.20
60	6.82	6.18	6.68	5.78	5.60	4.06
80	5.49	4.51	5.34	5.03	5.14	3.16
100	4.27	3.70	4.43	4.23	4.79	2.74

Table III Effect of Dye Concentration in Streaming Solution on Surface Charge Density of Different Polyester Fibers

Concentration of Dye Solution at pH 5 ($M \times 10^{-6}$)	(-ve) Surface Charge Density (e.s.u./cm ²)					
	Flat Filament NPET		Text-NPET		CDPET	
	Unset	Set	Unset	Set	Unset	Set
10	21.49	20.33	25.13	21.78	19.32	17.58
20	28.07	26.64	29.28	25.11	25.26	21.64
40	34.32	32.54	32.60	29.04	27.89	22.44
60	36.12	32.74	35.39	30.54	29.63	21.47
80	33.52	27.54	32.62	30.71	31.39	19.27
100	29.15	25.25	30.24	28.87	32.71	18.68

lution, a progressive decrease in the negative value of zeta potential of the fibers is observed, which could be attributed to the constant increase in the adsorption of positively charged dye ions (cations) on the anionic sites on the fiber surface. At a given concentration of cationic dye in the streaming solution, the heat-set sample gave a lower value for negative zeta potential. This was true for all the fiber samples. Heat-setting in the relaxed condition results in a decrease in specific surface area, since it causes an increase in denier due to relaxation shrinkage that is well known and substantiated by nominal linear density values obtained using the Vibroscope for unset and set samples (refer to Table I). This in turn may be responsible for lowering the negative zeta potential. In general, at a given concentration of cationic dye in the streaming solution, the CDPET gave the least value for negative zeta potential whereas Tex-NPET gave the maximum. This is obviously because of the increased anionic

nature and higher polarity of CDPET whereas Tex-NPET has a higher surface area as discussed earlier.

Results in Table III indicate that in general the surface charge density was found to increase with an increase in the concentration of dye in the streaming solution for unset as well as heat-set samples. This is due to an increase in the interaction between the anionic sites on the fiber and dye cations in and around the fiber surface and fiber-liquid interphase. However, a reversal in the trend occurred at a very high concentration of cationic dye in the streaming solution. This may be attributed to the changes in the electrical double layer and the multimolecular layer adsorption of the dye cations on the fiber surface at higher concentrations of dye in the streaming solution. For all the fibers, at a given concentration of dye in the streaming solution, the surface charge density values were higher for unset samples than those for heat-set samples, which is expected since the zeta potentials of the latter sam-

Table IV Effect of Dye Concentration in Streaming Solution on Surface Conductivity of Different Polyester Fibers

Concentration of Dye Solution at pH 5 ($M \times 10^{-6}$)	Surface Conductivity $\times 10^6$ (ohm ⁻¹ cm ⁻¹)					
	Flat Filament		Textured		Cationic Dyeable	
	Unset	Set	Unset	Set	Unset	Set
10	2.724	3.338	2.315	2.350	2.254	3.445
20	3.587	3.977	2.616	2.630	3.288	3.823
40	4.412	4.824	3.316	3.133	3.684	4.747
60	5.010	5.374	4.151	3.629	4.161	5.285
80	5.655	6.015	4.504	4.553	4.964	5.548
100	6.686	6.398	4.064	4.471	5.764	5.845

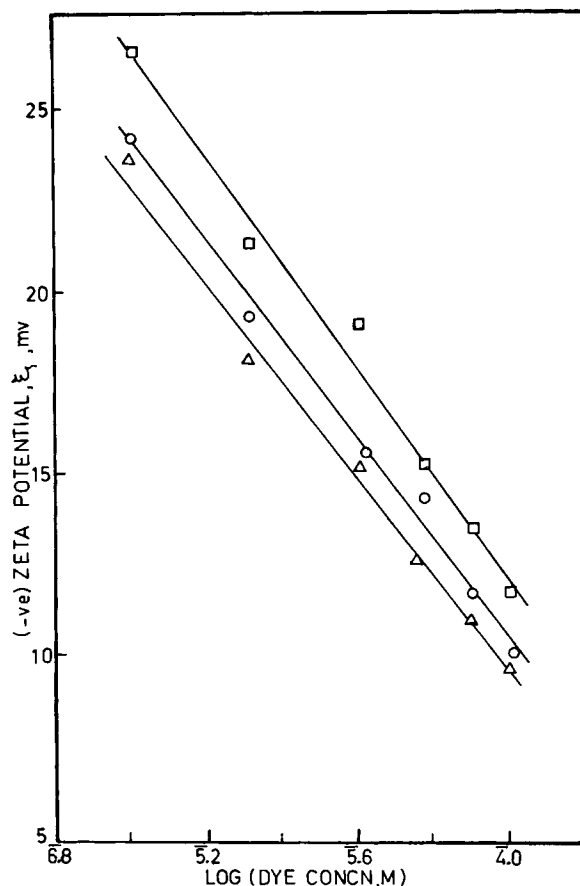


Figure 4 Relation between zeta potential and log (dye concentration): (○) NPET; (□) EDPET; (△) CDPET.

ples were lower than those of the former. At a given concentration of cationic dye in the streaming solution, the surface charge density values were found to be at a minimum for CDPET, indicating its maximum interaction with dye cations in the streaming

solution, maximally lowering the negative zeta potential.

The results in Table IV suggest that surface conductivity values of different polyester fibers were found to increase with the increase in concentration of cationic dye in the streaming solution. This could be attributed to the increase in the ionic interaction and ionic concentrations at and around the fiber-liquid interphase as the concentration of dye in the streaming solution was increased. At a given concentration of cationic dye in a streaming solution, surface conductivity of the heat-set sample was found to be more than that of the unset one and this may be attributed to a slight increase in carboxyl content, and hence polarity of the sample, as a result of heat-setting.

Set II: Effect of Cationic Dye Concentration in Streaming Solution on Electrokinetic Properties

This set involves the trio of flat filament fibers namely NPET (50^D/36), EDPET (50^D/40), and CDPET (50^D/24). Figure 4 indicates that with an increase in cationic dye concentration in the streaming solution, the negative zeta potential of the fiber decreases almost linearly, irrespective of the type of fiber. However, the absolute values of negative zeta potential for the three fibers differed distinctly.

At any given concentration of the dye in the streaming solution, it was found that CDPET exhibited the lowest zeta potential value whereas EDPET exhibited the highest. The more polar nature of CDPET coupled with its reduced surface area would be responsible for such behavior because the filament denier of this fiber is maximum as is also

Table V Effect of Nature of Polyester and Heat-Setting on Its Fineness and Specific Surface Area

Fiber Sample	Filament Denier	Nominal Linear Density by Vibroscope	Micronaire Values	Specific Surface Area (m ⁻¹)	Increase in Micronaire Value on Heat-Setting (%)	Decrease in Specific Surface Area on Heat-Setting (%)
NPET	1.388 (1.505)	1.53 (1.70)	4.95 (5.35)	0.449K ^a (0.432K)	8.1	3.8
EDPET	1.250 (1.425)	1.31 (1.42)	4.45 (4.80)	0.474K (0.456K)	7.9	3.4
CDPET	2.083 (2.438)	2.12 (2.52)	6.85 (7.25)	0.382K (0.371K)	5.8	2.8

Values in parentheses are to heat-set sample.

^a K, constant.

the nominal linear density as measured by a Vibroscope (Table V). Micronaire values also indicate the lower surface area of CDPET.

In the case of EDPET, these zeta potential values were found to be more than those of NPET at any given concentration of dye in the streaming solution. This could be attributed to the least filament denier of EDPET and also the nominal linear density values. Micronaire values support the maximum surface area of EDPET.

The surface charge density values for EDPET were found to be maximum and for CDPET minimum at any given concentration of the dye in the streaming solution (Fig. 5). This was parallel in trend to the negative zeta potential of the fibers. However, with an increase in dye concentration in the streaming solution, the surface charge density values increased progressively, showing a levelling-off tendency at a very high concentration of dye in the streaming solution.

Figure 6 suggests that surface conductivity was found to increase with increasing dye concentration in the streaming solution. However, very little influence of the nature of polyester on this property was observed and all three curves for the three different polyester fibers almost coincided. The surface conductivity of the fiber was also related to the dye cations present in the fiber-liquid interphase and hence, its enhancement with higher concentration

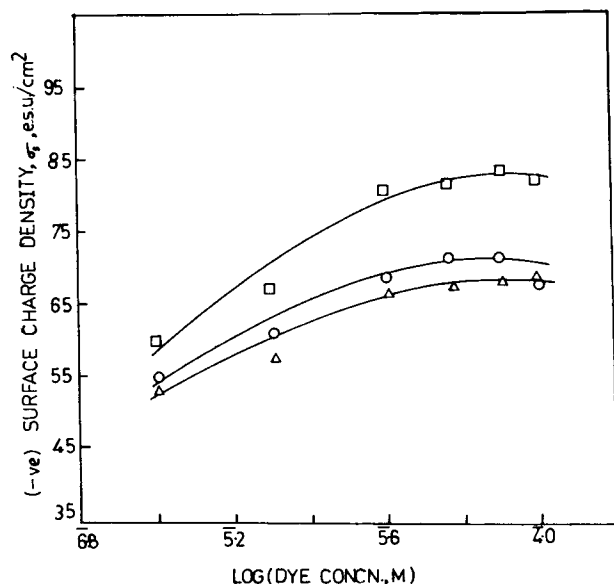


Figure 5 Relation between surface charge density and log (dye concentration): (○) NPET; (□) EDPET; (△) CDPET.

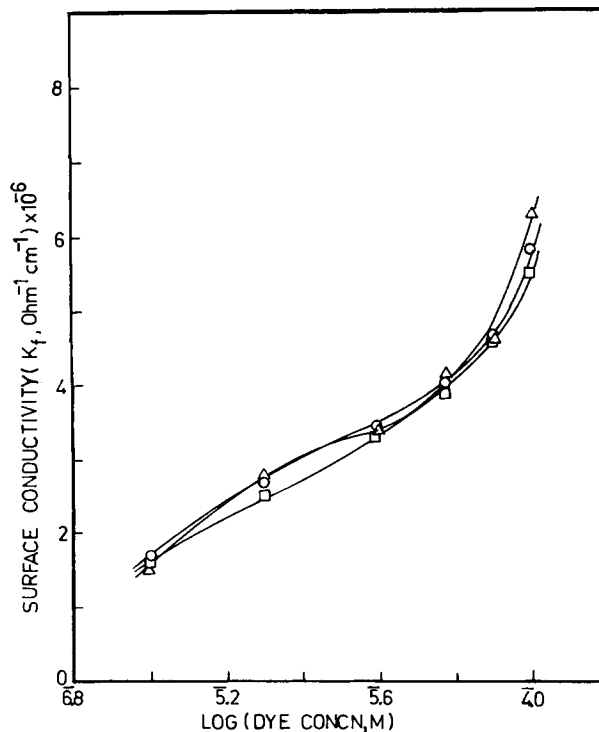


Figure 6 Relation between surface conductivity and log (dye concentration): (○) NPET; (□) EDPET; (△) CDPET.

of dye in the streaming solution would be quite obvious.

These differentially dyeable fibers are always accompanied by normal polyester in the fabric state and hence, all being thermoplastic in nature, require heat-setting for dimensional stability. Consequently the effect of heat-setting of different types of polyester on electrokinetic properties needs to be studied. It is with this view in mind that the above mentioned trio of polyester yarns was subjected to heat-setting in the relaxed condition at 180°C for 90 s. Plugs of such heat-set fibers were then subjected to measurement of zeta potential, surface charge density, and surface conductivity. The results relating zeta potential with concentration of cationic dye in the streaming solution at pH 5, are given in Figure 7. It is clear from these results that, although the general trend of the decrease in the zeta potential with increase in the dye concentration remained the same, the actual value of negative zeta potential at any given concentration of dye in the streaming solution was much lower for the heat-set sample than for the corresponding unset sample. In other words, relaxed heat-setting brought about lowering of zeta poten-

tial, which may be attributed to the reduction in the surface area of the fiber. It has been observed that during relaxed heat-setting, the diameter of the fiber or individual filament increased and therefore the surface area per unit volume of the fiber would decrease. This is further confirmed by an increase in denier of polyester filaments as a result of heat-setting (Table V). The changes in the zeta potential as a result of heat-setting may be attributed to changes in surface area of these fibers. Nominal linear density values also confirm these results supported further by micronaire values and surface area predicted by these values. There was a clearcut decrease in surface area observed as a result of heat setting that was mainly responsible for lowering negative zeta potential. Although individually each of these fibers showed a decrease in zeta potential as a result of heat-setting, Figure 7 suggests that, at lower dye concentration, CDPET exhibited zeta potential values in between the values for EDPET and NPET, when zeta potential values of heat-set samples were compared. This can be understood because

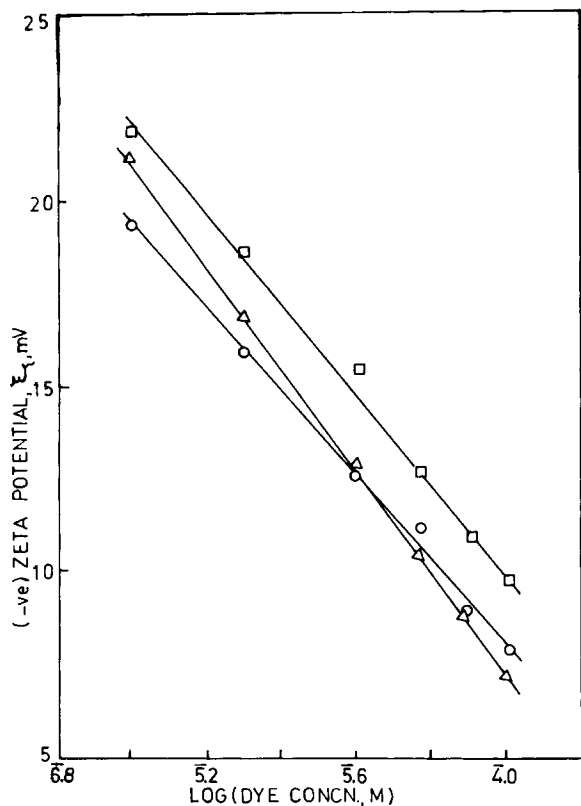


Figure 7 Relation between zeta potential of heat-set fibers and log (dye concentration): (○) NPET; (□) EDPET; (△) CDPET.

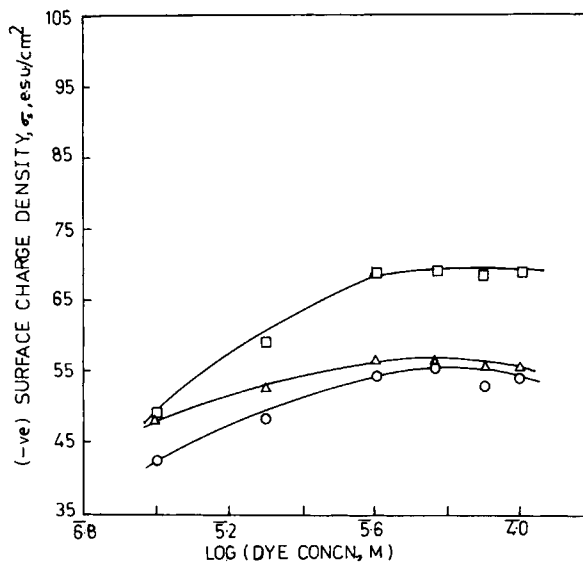


Figure 8 Relation between surface charge density of heat-set fibers and log (dye concentration): (○) NPET; (□) EDPET; (△) CDPET.

the decrease in zeta potential in CDPET as a result of heat-setting was much less than that in NPET.

As far as the surface charge density (Fig. 8) and surface conductivity (Fig. 9) were concerned, the

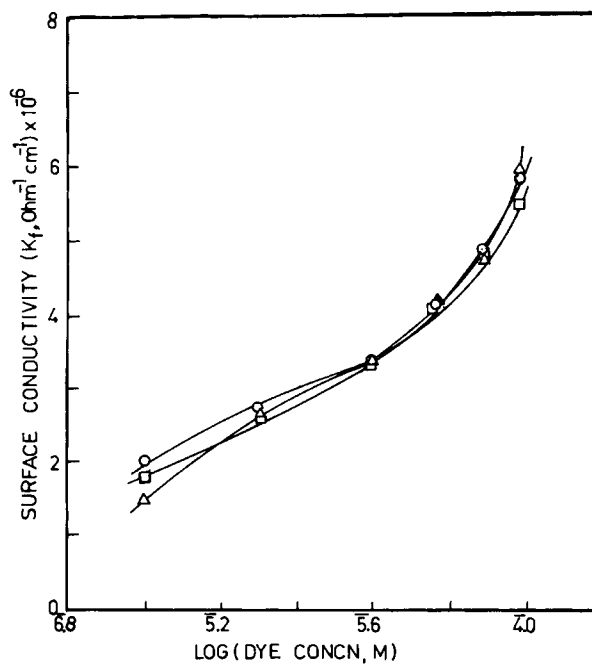


Figure 9 Relation between surface conductivity of heat-set fibers and log (dye concentration): (○) NPET; (□) EDPET; (△) CDPET.

trends observed were similar to the earlier case although actual values were different.

CONCLUSION

The differentially dyeable as well as textured polyester fibers do show variation in interaction with dye cations as well as H-ion in the streaming solution resulting in varied electrokinetic properties. The higher polarity and reduced surface area of CDPET are the main factors providing reduced zeta potential. As a result of relaxed heat-setting, all these fibers exhibit lowering of zeta potential, which may be attributed to reduced specific surface area. However, the degree of reduction of zeta potential as a consequence of heat-setting remained very much a function of the nature of these fibers and their surface area.

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