Improving Dyeability of Polyester by Modifying Polymer and Fibre Structure

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Abstract: ***Production of polyester fiber is increasing throughout the world. When this fiber was introduced as a textile material, a lot of problems were faced during dyeing. This was due to the crystalline and hydrophobic nature of the fiber and there is no chemically active group in this fiber. Polyester fiber is mostly dyed with disperse dye using conventional methods of dyeing which faces a lot of problem. To solve this problem different methods of dyeing are given in this paper. The dyeability of the polyester fiber can be improved by modifying the polymer and fiber structure. Carrier free dyeable polyester can be prepared by incorporating additives such as polyethylene glycol, Azilic acid, Adipic acid, etc. and also by manipulating the spinning speed and drawing and heat setting parameters.***

Keywords: Carrier dyeing, Thermosol process, High temperature, High pressure dyeing, Azilic acid

1.Introduction

One of the important advantages of polyester fibres is that its properties can be tailor-made to suit the requirements of the consumers. Thus the dyeability of polyester fibre can be altered at will to satisfy the needs of the fabric manufacturer or the actual user. By making appropriate changes in the polymer and fibre structure it is possible to prepare polyester fibre having dyeability with disperse dyes or cationic dyes. Similarly a fibre which can be dyed at boil without carrier can be also prepared by the above approach. Let us first analyse why there is a need to modify the dyeability of normal dyeable polyester fibre and then review various methods available to modify the dyeability of polyester.

Difficulties in Dyeing of Conventional Polyester Fibre

When polyester fibre was first introduced as a textile material considerable difficulties were encountered in dyeing of this fibre (1). Three factors are responsible for making polyester fibre difficult to dye. These are (1) It is highly crystalline; (2) It is markedly hydrophobic and (3) It has no chemically active group.

On account of these reasons polyester fibre cannot be dyed with dyestuffs that are generally employed for dyeing cellulosic or protein fibres.

Polyester fibre is mostly dyed today with disperse dyes (2). These dyes are water insoluble and are applied in the form of an aqueous dispersion. The mechanism of dyestuff in the organic fibre. However, some investigators believe that the dyestuff is not dissolved in the fibre but is only mechanically entrapped within it.

Disperse dyes were initially developed for dyeing of cellulose acetate. Since ester group content of cellulose acetate and polyester fibre are nearly the same (40-45%) attempts were made to dye polyester fibre with disperse dyes by the method similar to the one which was used for dyeing cellulose acetate. However, it was observed that polyester fibre could not be dyed with disperse dyes at a temperature of 80-100 °C This was due to very slow rate of diffusion of disperse dyes into compact polyester fibre as can be seen from table 1. It is quite evident that the rate of diffusion of Dispersol Fast Orange G in polyester fibre is extremely slow, both at 85 and 100 °C as compared with the rate of diffusion in cellulose acetate and nylon.

Table 1: Rate of Diffusion of Dispersol Fast Orange G in Different Fibres

Fibre	Dyeing Temperature °C	Rate of Diffusion
Polyester	85	1
Polyester	100	48
Nylon 66	100	680
Acetate	85	460

Thus, dyeing of polyester fibre with disperse dyes using conventional machinery operating at maximum temperature of 95-100 °C was found to be impossible.

Considerable amount of research work was carried out to solve the problem of dyeing of polyester fibre, which had ultimately resulted in the development of three important methods of application of disperse dyes to this fibre. The three methods are (a) Carrier dyeing; (b) High temperature dyeing and (c) Thermosol process.

Although these three methods are used at present for dyeing normal polyester fibre, there are certain drawbacks associated with these three dyeing methods. These drawbacks are (a) high consumption of energy; (b) water pollution problem and (c) difficulty in getting fancy coloured fabrics. In order to solve these problems various modified polyester fibres are being developed by modifying the polymer and fiber structure. The important modified polyester fibres are (i) Carrier-free dyeable polyester and (ii) Cationic dyeable polyester.

(i) Carrier –Free Dyeable Polyester

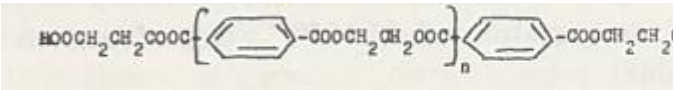
Conventional polyester fibre can be dyed either at 120-130 °C in pressure dyeing machines or at boiling point temperature in the presence of a carrier. The first method requires special dyeing machines and considerable amount of energy. The second method requires expensive carriers which also cause water pollution and yield an unsatisfactory quality of dyed goods. Carrier-free dyeable polyester is recently developed, and can be dyed at boil with disperse dyes in the absence of carrier (3-6). Thus, dyeing can be carried out in simple machines with considerable saving in energy and avoiding the problems of carriers.

Two approaches are available for preparing carrier-free dyeable polyester fibre. These are;

(1) Modification of polymer and
(2) Modification of fine structure of fibre using normal poly (ethylene terephthalate) polymer.

2.Modification of polymer

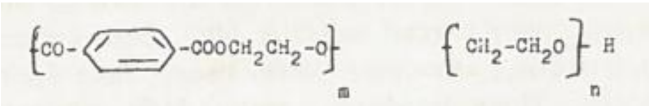
Normal dyeable polyester fibre is prepared by using dimethyl terephthalate (DMT) or terephthalic acid (TPA) and monoethylene glycol (MEG) as raw materials.



Normal dyeable polyester

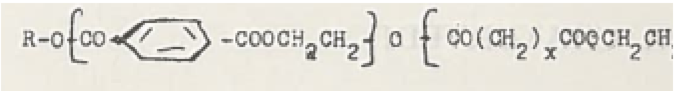
Carrier-free dyeable polyester is prepared by modifying the polymer by adding certain additives such as polyethylene glycoi, adipic acid, azilic acid, etc.

For example a fibre having blocks of polyethylene terephthalate and polyethylene glycol is carrier-free dyeable.



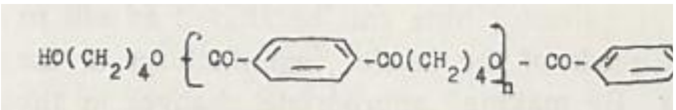
Block A (PET) Block B (PEG)

Similarly dicarboxylic acid modified polyethylene terephthalate fibre can be also dyed witrh disperse dyes at boil without carrier.



Carrier free dyeable polyester fibre can be also prepared using entirely new polymer i.e.

Polybutylene terephthalate (PBT). The PBT polymer is prepared from DMT or TPA and butylene glycol (1, 4 butane diol).



Polybutylene terephthalate

The PBT based fibre has a lower melting point (225-230 °C) and is generally used for making car pets.

Using this approach of polymer modification a number of fibre manufacturing Companies are producing carrier-free dyeable polyester fibres. Typical commercial fibres are Diolene 742 and Diolene 42 (Enka Glanzstoff AG), Kodel V (Eastman Chemical Products Co), F11 type 405 (Celanesa Fibre Marketing Co.), Trevira 210, 310, 630 (Hoechst) etc. The glass transition temperature T_g of these fibres is about 10°C lower than the normal dyeable polyester. The diffusion of the disperse dyes in these fibres is faster and hence deep shades can be dyed at boil even in the absence of carriers.

These fibres are suitable for blending with wool or cotton. Since blends of carrier-free dyeable polyester fibre and wool can be dyed at boil, the degradation of wool, which occurs when dyeing is carried out at 115-120 °C is eliminated. The blends of carrier-free dyeable polyester and cotton possess a better feel than blends of normal dyeable polyester ester and cotton.

The technological data of various types of carrier-free dyeable polyester fibres is given in Table 2.

The dyeability of normal dyeable polyester and carrier-free dyeable polyester is shown in Figure 1. It can be seen that the relative colour depth on carrier-free dyeable polyester is much higher than the normal dyeable polyester fibre at 100 °C. Approximately the same depth of shade is obtained on carrier free dyeable polyester on dyeing at boil without carrier as obtained on dyeing normal dyeable polyester at 125 °C, or at boil in presence of a carrier.

Levelness of the shade on carrier-free dyeable polyester can be a problem if proper precautions are not taken during dyeing. This is due to the fact that the fibre has high affinity for dispersing dyes and the exhaustion of the dye from the dyebath is very rapid. With fast exhausting dyes, localized absorption of dye may occur in the boundary zone between the fibre surface and dye liquor, unless a uniform concentration gradient is assured, for instance by rapid dye liquor circulation or high fabric speed. The dye exhaustion can be also optimised by using proper temperature control programme. The heating of dyebath above 60°C should be slow to avoid unlevelness. The light fastness of disperse dyes on carrier-free dyeable polyester is slightly lower than that on normal dyeable polyester but is adequate for outerwear goods. The fastness to washing is also somewhat lower than on normal dyeable polyester. The appropriate instructions should be given to consumers for washing the carrier-free dyeable goods at temperature below 50 °C.

Preparation of Carrier-free Dyeable Polyester Fibre from Unmodified Poly (Ethylene Terephthalate) Polymer

During the last few years attempts were made to prepare carrier-free dyeable polyester fibre from unmodified poly (ethylene terephthalate) polymer by making certain changes in melt spinning, stretching, stretching, and heat setting operations. Thus, the crystallinity and orientation of the fibre is adjusted to get fibre with good dyeability at boil (7).

According to Vassilatos et. Al (8) the dyeability of polyester yarn spun at a speed of 6400 m/min. is 3.5 times higher than that of yarn spun at 915 m/min. and subsequently drawn to a draw ratio of 3.5. Jacob and Schroder (9) have reported that polyester yarn spun at a speed of 5000 m/min. can be

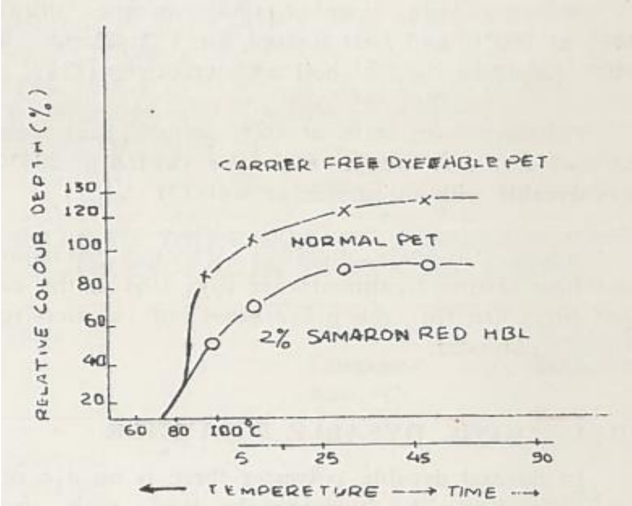


FIGURE 1 RELATIVE COLOUR DEPTH OF NORMAL PET AND CARRIER FREE DYEABLE PET

Table 2: Technological Data of Various Types of PES Fibres

°C PES-Fibres	Density (g/cm3)	Melting point Strength	Elon-crease ob-Shrink-°C (cN/tex)	gation ration (%)	age at (strokes)	The boil (%)
Normal Dyeable types						
Cotton-types	1.38	256	55-65	15-25	3000-6000	3
Wool-type	1.38	256	40-50	35-55	2500-3500	1
Low pilling types	1.38	256	20-35	20-50	150-2500	1
Carrierless dyeable Types						
Test fibre 1	1.38	256	30-40	40-58	1800-3500	1
Test fibre 2	1.35	240	22-45	25-60	1500-3500	3
Test fibre 3	1.32	224	25-40	30-60	2000	2

Dyed without carrier to the same shade as the yarn spun at 200 m/min. and drawn, with carrier.

Polyester yarn melt spun at 3300 m/min, heat treated at 180°C for 0.09 sec. and drawn subsequently 40% at 115 °C could be dyed at boil without carrier (10).
Polyester yarn spun at 4000 m/min. speed, heat treated for 0.79 seconds at 250 °C drawn 31 % and false twisted at 200°C could be dyed at boil without carrier to a deep shade (11).

Polyester yarn spun at 1500 m/min, drawn 24% at 160°C and heat treated for 1.2 seconds at 280 °C could be dyed at boil without carrier (12).

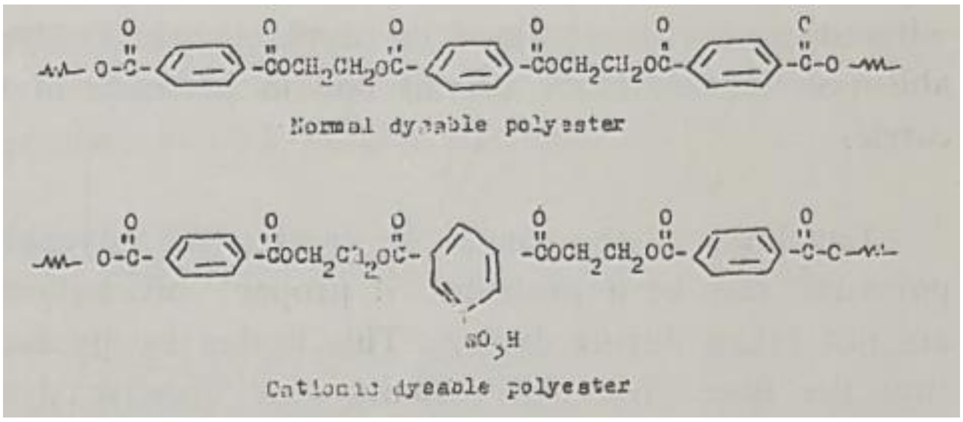
Polyester yarn spun at 4600 m/min, heat treated at 240 °C and drawn and false twisted at 203 °C was dyeable without carrier at boil (13).

A number of such modified spinning, stretching and heat setting treatments are suggested in the patent heat setting treatments are suggested in the patent literature for the preparation of carrier-free dyeable polyester.

(II) Cationic Dyeable Polyester

In normal dyeable polyester there is no dye site for ionic dyes. So it cannot be dyed with dyes other than disperse dyes.compared to ionic dyes, disperse dyes have smaller molecular extinction coefficients and lower build up property, so disperse dyes cannot give vivid and deep colours. Fastness to sublimation and fastness to wet treatments of disperse dyes are relatively poor compared with other classes of dyes. In order to solve these problems, cationic dyeable polyester fibre was prepared by modifying the polymer structure of poly (ethylene terephthalate) using additive containing sulfonic acid groups (14-16).

Many additives are recommended in the literatuer such as dimethyl ester of 5-sulfoisophthalic acid, 4-sulfo phenyl, 4, 5-dicarboyethoxybenzene sulfonate, etc. Because of the presence of sulfonic acid groups, the cationic dyeable polyester fibre can be dyed with cationic dyes. The benzene ring in the additive is tilted and hence crystallinity of cationic dyeable polyester fibre is lower than nomal dyeable polyester fibre.



Cationic dyeable polyester fibre was first developed by Du pont in 1962 under the trade name Decron T-64. The fibre is now well established commercially and accounts for about 15% of the total world production of polyester fibre. It is presently manufactured by most of the leading polyester producers and offers the following advantages (14):

1. Attractive fancy shades can be produced by blending cationic dyeable polyester fibre with regular dyeable polyester fibre and wool or celulosic fibres and dyeing in the cloth form. Until recently such fancy shades were produced by dyeing in loose fibre or yarn form. However the fabric dyeing is always preferred to loose fibre or yarn dyeing due to the following reasons-(a) in the case of loose fibre dyeing, matting presents a great problem as it is very difficult to separate the individual fibres after dyeing; (b) the rewinding costs necessary in yarn dyeing are eliminated. In general, cost of dyeing in the fabric form is always less than that of dyeing loose fibre or yarn dyeing; (c) all kinds of colour combinations can be produced from the same raw material, thereby eliminating the storage of the goods can be easily attended; (e) the dyer can offer to the trade an unlimited number of colour combinations. Special shades can be produced without additional loss of time.
2. Cationic dveable polyester can be used individually to obtan very bright shades. This is of great advantage especially in ladies' wear and in double knits, where brilliant colours are required. Which are unattainable with disperse dyes.
3. Cationic dyeable polyester is useful is minimising the problem of frosting in polyester/ cellulosic blends, dyed in contrast shades. Frosting occurs because of the difference in abrasion resistance of polyester and cellulosic fibres. The cellulosic fibres have much lower abrasion resistance than polyester. Hence, during wear, part of the cellulosic portion is remoed, leading to patchy dyed appearance at that particular portion.

In order to minimize frosting, cationic dyeable polyester is used in combination with regular dyeable polyester and cellulosic fibres. Thus, a blend containing 33% cationic dyeable polyester, 33% disperse dyeable polyester and 34% cotton is prepared. By dyeing dyeable polyester to the lightest shades, cationic dyeable polyester to the deepest shades, and the cotton portion to an intermediate shade, the frosting can be minimized. For example, the production of a contrast shade of deep brown and light blue requires the dyeing of disperse dyeable polyester to a light blue shade, cationic dyeable polyester to a deep brown shade and cotton to a composite of deep brown and light blue shades.

(i) Because of lower tenacity, cationic dyeable polyester pills less than normal dyeable polyester.

The tenacity of cationic dyeable polyester fibre is compared with that of normal dyeable polyester in Figure 2 (15). The dyeability of cationic dyeable polyester fibre is much better than normal dyeable polyester but is less than that of acrylic fibre as can be seen from Figure 3 (15).

Dyeing of Cationic Dyeable Polyester Fibre

Cationic dyeable polyester fibre is generally dyed with cationic dyes in HT dyeing unit at a temperature

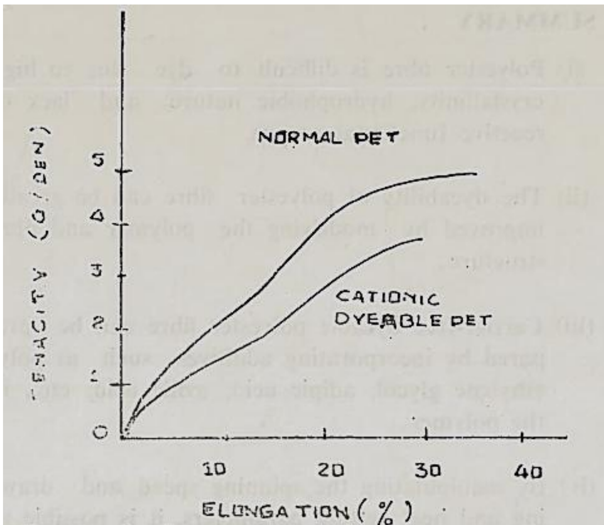


FIGURE 2 - TENACITY AND ELONGATION (%) OF NORMAL PET AND CATIONIC DYEABLE PET

Of 110-115 °C. If the dyeing is done at boil it is necessary to add a carrier. Dyeing of cationic dyeable polyester at temperature above 120 °C is not recommended, as fibre gets degraded at high temperature.

Cationic dyeable polyester fibre can also be dyed with disperse dyes and it gives about 10-20% higher colour yield as compared with normal dyeable polyester in deep shades, due to its open fibre structure. Since cationic dyeable polyester is mostly used in preparing blended fabrics, proper selection of disperse dyes is important to get appropriate shade.

Cationic dyes should be selected from the point of view of their fastness properties. The wash and rubbing fastness of cationic dyes on cationic dyeable polyester is good. The light fastness of the dyes varies from 3-7 depending upon the dyes (Table 3). (15).

Proper selection of cationic dyes to get light fast shade is thus important.

Development of Cationic Dyeable polyester fibre which is Dyeable at Boil without Carrier

The first generation cationic dyeable polyester fibre was useful in getting bright shades and multicoloured fabrics when blended with normal dyeable polyester and cotton or wool. However, for dyeing this fibre it was necessary to have high temperature high pressure (H. T. H. P.) dyeing machine. During

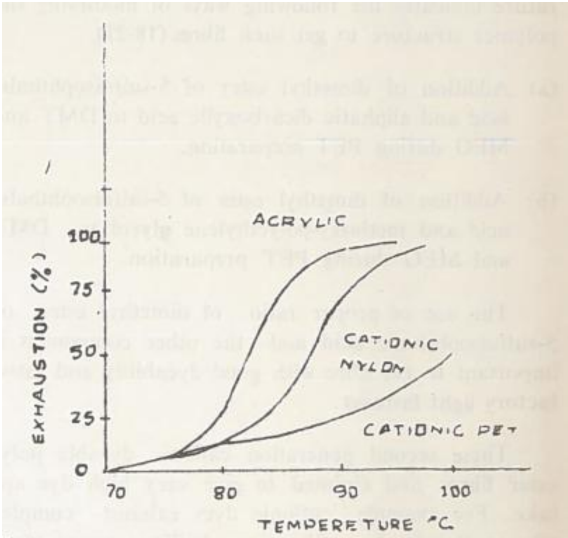


FIGURE 3 - DYEABILITY OF ACRYLIC, CATIONIC DYEABLE NYLON AND CATIONIC DYEABLE POLYESTER

Table 3: Fastness Properties of Cationic Dyes on Cationic Dyeable polyester

Dye CI Basic	Light fastness (Fadometer)	wash fastness ISO test No.3	Rubbing fastness	Sublimation temperature
				°C
Yellow 38	4-5	5	5	220
Yellow 39	5-6	5	5	220
Orange 35	5-6	5	5	220
Orange 36	6-7	5	5	220
Red 58	5-6	5	5	220
Red 64	6-7	5	5	220
Violet 37	6-7	5	5	220
Violet 39	3-4	5	5	220
Blue 71	4-5	5	5	190

The last ten years number of fibre manufactures undertook research work to prepare cationic dyeable polyester fibre, which can be dyed at boil without carrier. Some of the successful second generation products developed are calafine by toyobo Co., YD-20 by Unitika, plus-20 by mitsubishi rayon Co., and so on (17). The method of preparation of these fibres is not disclosed. However, patent literature indicates the following ways of modifying the polymer structure to get such fibres (18-21).

(a) Addition of dimethyl ester of 5-sulfoisopthaslic acid and aliphatic dicarboxylic acid to DMT and MEG during PET preparation.
(b) Addition of dimethyl ester of 5-Sulfoisophthalic acid and MEG during PET preparation.

The use of proper ratio of dimethyl ester of 5-sulfoisophthalic acid and the other component is important to get fiber with good dyeability and satisfactory light fastness.

These second generation cationic dyeable polyester fibers and claimed to give very high dye up-take. For example cationic dyes exhaust completely on Calafine fibre at boiling temperature whereas in normal cationic dyeable polyester the exhaustion is about 95% even at 120 ^{0}C (22). Thus, water pollution problem is not created during dyeing of calafine is about 84% at boil as compared with the exhaustion of about 75% on normal cationic dyeable polyester fibre at 120 ^{0}C.

The modified cationic dyeable polyester fibre will give considerable saving in energy cost.

3.Summary

1. Polyester fibre is difficult to dye due to high crystallinity, hydrophobic nature and lack of reactive functional groups.
2. The dyeability of polyester fibre can be greatly improved by modifying the polymer and fibre structure.
3. Carrier-free dyeable polyester fibre can be prepared by incorporating additives such as polyethylene glycol, adipic acid, azilic acid, etc., in
4. By manipulating the spinning speed and drawing and heat setting parameters, it is possible to get carrier-free dyeable polyester fibre.
5. Cationic dyeable polyester is prepared by incorporating dimethyl ester of 5-sulfoisophthalic acid in the polymer. This fibre is useful in preparing multicoloured fabrics.
6. Second generation cationic dyeable polyester fibre is developed which are dyeable at boil with cationic dyes.

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