

The Effect of Dyes and Dyeing on the Mechanical Properties of Polymeric Materials

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Synopsis

The effect of reactive and disperse dyes and dyeing on the mechanical properties of cotton and polyester fibers, respectively, has been studied. It is observed that reactive dye (Procion Brilliant Red MX-2B) and disperse dye (Dispersol Red B-2B) caused a decrease in the tensile strength of the fiber which was often accompanied by a decrease in the extensibility and general improvement in the tensile stiffness of the fibers. A linear relationship exists between percent disperse dye on the fiber and the square root of time of dyeing for poly(ethylene terephthalate) fibers in the initial region of dye uptake.

INTRODUCTION

The dyeing of textile fibers involves the application of a colorant which is of comparative permanence or fastness. Thus, in dyeing it is required that the dye be associated strongly with the fiber to make it resistant to such agents as water, detergents, perspiration, weather, solvents, etc. Generally, dyes can be attached to textile fibers in one of the following ways¹: (i) ionic forces, (ii) covalent bonding, (iii) hydrogen bonding, (iv) van der Waals forces. Van der Waals forces are the weakest and are thought to be responsible for the poor substantivity of some direct and vat dyes that have extended π -electron system.² The dyeing of wool, silk, and acrylic fibers with acid and basic dyes is due mainly to the formation of salt-type links between the dyes and the fibers. Dyes that attach themselves to the substrate through covalent and hydrogen bonding are those of interest in this investigation.

Man-made polymeric substrates such as poly(ethylene terephthalate), polypropylene, and cellulose triacetate contain a very low concentration of ionic groups; and, compared with naturally occurring polymers, they are hydrophobic. The low water absorption of these polymers reflects low swelling, and hence they are permeable to only small dye molecules. In order to dye such fibers, weakly polar dyes of relatively low molecular weight were developed. The lack of ionic solubilization of these dyes led to sparing aqueous solubility; and when they are applied in aqueous systems they are present, initially, as dispersions, hence the name disperse dyes.⁶ Bird, Manchester, and Harris⁵ have suggested that disperse dyes bind onto sites in the fiber by hydrogen bonding. Similar conclusions were drawn by Shuler and Remington⁹ even though they also suggested that absorption sites may not be present.

Covalent bonding is predominantly characteristic of the reactive dyes. An examination of the theory of dyeing with reactive dyes reveals that the three major factors that may influence dyeing behavior are (i) the chemical reactivity of the dye, (ii) the rate of diffusion of the dye, and (iii) the affinity of the dye. It

is imperative, therefore, that in attempting to give colors of comparative permanence to textiles, those properties that make textile fibers useful should not be destroyed. It has been established that dye-fiber interactions are accompanied by changes in the mechanical properties of the fiber. Investigations¹⁰ on the effect of dyes on the mechanical properties of wool have shown that the strength of wool decreased when dyed; and as the amount of dye on the fiber increased, the strength and elongation decreased. With nylon 66, Dical (cellulose acetate), and Fibrolene (casein fiber), it has been shown¹⁰ that there is generally an increase in the initial modulus and the breaking strength after dyeing the fibers.

In the investigation reported in this paper, the effects of a disperse dye and a reactive dye on the mechanical properties of polyester fiber, poly(ethylene terephthalate), and cellulosic substrates, respectively, were studied.

EXPERIMENTAL

Materials

Bleached cotton fabrics and poly(ethylene terephthalate) (PET) fibers were supplied by Kaduna Textiles Limited (K.T.L.), Kaduna, and Nichemtex Industries, Ikorodu, respectively. The dyestuffs, Procion Brilliant Red MX-2B (C.I. 18158) and Dispersol Red B-2B (C.I. 62015), were supplied by Chemical and Allied Products Limited, Lagos. The chemical structures of Procion Brilliant Red MX-2B and Dispersol Red B-2B are shown in Figures 1(a) and 1(b), respectively.

Dyeing Methods

Dyeing of bleached cotton with Procion Red MX-2B (C.I. 18158) was carried out in a five-neck FR3L culture flask at a constant temperature of 35°C. The samples of bleached cotton fabric, 5–7 g each, were first treated with hot water to remove residual fillers and the pH adjusted to 7 with small amounts of acetic

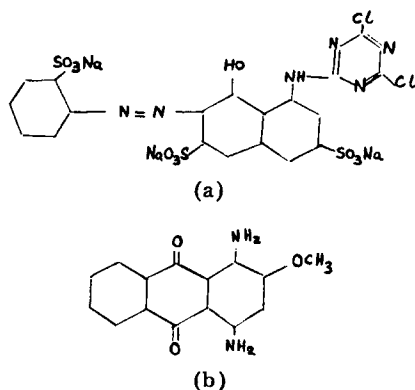


Fig. 1. Chemical structure of: (a) Procion Brilliant Red MX-2B (C.I. Reactive Red 1, C.I. No. 18158); (b) Dispersol Red B-2B (C.I. Disperse Red II, C.I. No. 62015).

acid. The dye bath was set at 35°C and the fabrics dyed to 0.2, 0.5, and 1.0% shades, using a liquor ratio of 50:1. The predissolved dyes were added and the fabrics dyed for 15 min; sodium sulfate, 40 g/l. for shades up to 0.5% and 50 g/l. for deeper shades, was added in portions over 50 min. The soda ash (10 g/l. for shades up to 0.5% and 15 g/l. for higher shades) was added in the 60th min. Dyeing was continued for further 60 min. Total dyeing time was 120 min.

Rinsing and washing off were carried out at the boil for 20 min in a bath containing 1 g/l. of Lissapol ND (nonionic surfactant), and the fabrics were squeezed and dried at room temperature.

Dyeing of the PET fibers was carried out in the culture flask with a dispersion of 1.0 g of the Dispersol Red B-2B dyestuff (C.I. 62015) in 1 liter distilled water. About 3–4 g PET samples were introduced into the dyeing flask at 50°C and then dyed at a temperature of 100°C. Samples were removed at the 4th, 16th, 36th, 64th, 100th, and 144th minute. The samples were dyed in batches of two and were rinsed in hot and then in cold water after dyeing. All dyed samples were air dried at room temperature.

Quantitative Determination of Fixed Dyes

Determination of Procion Dye on Cotton. The dissolution of reactive dyes was studied in a modified cadmium–ethylenediamine complex solvent which has the advantages of being colorless, easy to prepare, and of high stability. The composition and properties of the cadmium–ethylenediamine complex (cadoxen) used are ethylenediamine, 28%; cadmium hydroxide, 5%; sodium oxide, 0.5*M*; color, colorless; density, 1.077 g cm³ pH, 13.5. Finely divided reactive-dyed cotton, 0.20 g, was dissolved in 20 cm³ cadoxen by constant shaking for 24 hr. The dye solution was collected in a 100-cm³ volumetric flask, and the extraction procedure was repeated twice to obtain dye-free fibers. After collecting all the extracts and diluting up to the mark, the absorbance of the dye solutions was determined using Pye Unicam model SP6-200 spectrophotometer. The amount of dye fixed on each sample was read off from the calibration curve.

Determination of Disperse Dye on PET. Dyed PET fibers, 1.0 g, was treated with three 10-cm³ portions of dimethylformamide and adjusted to pH 4 with *p*-toluenesulfonic acid.⁷ This was considered to be sufficient for accurate results since temperature of the oil bath was 100°C and the heating time was only 1 min. The extraction flask was loosely covered during extraction to minimize oxidation. The extracts were diluted with acidified DMF to the mark in a 50-cm³ volumetric flask. The absorbance of each extracted dye was measured on an SP6-200 spectrophotometer and the actual amount of dye on the fiber was read off from the calibration curve. The calibration curve was prepared by plotting dye absorbances against several known dye concentrations.

Measurement of Mechanical Properties

Five samples of cotton and PET fibers were withdrawn from each sample of the undyed and dyed fabrics and tested on the Instron tensile tester. For the cotton yarns a gauge length of 10 cm and a chart speed of 10 cm/min and a cross-head speed of 5 cm/min were used, while the PET fibers were tested with a chart and cross-head speeds of 5 cm/min, respectively, using a 1-cm gauge length.

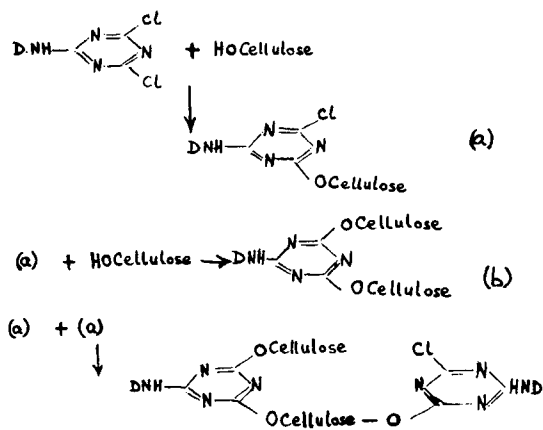


Fig. 2. Reaction between reactive dye and cellulose; D = dye.

All measurements were carried out at 70% relative humidity and 20°C. The specific stress, percent extension at break, initial modulus, and secant modulus at break were determined.

RESULTS AND DISCUSSIONS

Effect of Procion Dye on the Tensile Properties of K.T.L. Bleached Cotton

Procion is a reactive dyestuff which, under the conditions of application, enters into chemical combination with the substrate, a covalent bond being formed as shown in Figure 2. The effect of the covalent bond between dye and the cotton fiber leads to noticeable changes in the mechanical properties of the fiber as detailed in Table I. The general trend of results is consistent with reports of investigations¹⁰ on the mechanical properties of cotton which showed that the breaking strength decreased on dyeing. It is found, however, that the tensile

TABLE I
Properties of Procion-Dyed Cotton Yarn using the Cold Soda Ash Method

Dye absorbed, %	Specific stress, g/tex	Extension at break, %	Initial modulus, g/tex	Secant modulus at break, g/tex
0.0 (undyed)	14.3	13	150	1.1
0.2	14.1	11	183	1.3
0.5	13.2	10	200	1.32
1.0	9.7	9	233	1.07
2.0	10.8	8	275	1.35

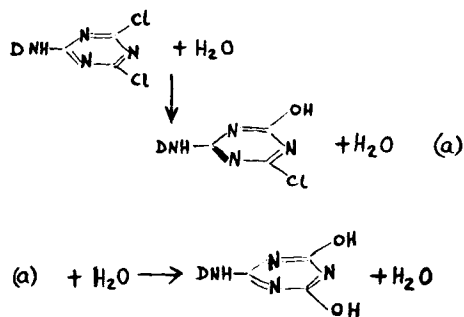


Fig. 3. Hydrolysis of a dichlorotriazinyl dye; D = dye.

strength may be attributed to both the decrease in degradation of cellulose and to breaking of internal structural elements.

A marked decrease in the percent extension at break is observed for unfinished cotton fabric after dyeing and the elongation further decreases as more dye is absorbed. However, one of the reactions of the dichlorotriazinyl dyes with cellulose is such that there is a possibility of crosslinking as detailed in Figure 2(b). It has been suggested¹⁰ that the formation of crosslinks will change the character of mercerized cotton fibers in such a way that the elongation will be decreased. Weiss et al.¹¹ have also shown that single cotton fibers that have been modified by crosslinking treatments show a decrease in elongation and a decrease in tensile strength with increasing crosslinks. The observed decrease in percent extension at break in this work would therefore indicate that some degree of crosslinking may have occurred during the dyeing process.

As shown in Table I, the application of reactive dyes to cotton resulted in the improvement of the initial modulus. Initial modulus is a parameter that clearly quantifies the resistance to stretching of the fiber to external stress and strain and describes the behavior of that material in the initial portion of the stress-strain curve. An improvement in the initial modulus generally leads to some increased fiber rigidity. It is known¹⁰ that crosslinking causes an increase in the initial modulus of dyed cotton fibers. Thus, the initial modulus result further lends support to the view that some crosslinking has taken place during the dyeing of cotton with reactive dyes.

Effect of Disperse Dye on the Tensile Properties of PET Fiber

The weakness of the bond between disperse dyes and PET fibers is reflected by the relative ease with which the dye is extracted from the dyed material.⁴ However, the formation of the bond between the dye and the fiber affects the mechanical properties of the fibers as shown in Table II.

The results indicate that initially dyeing causes a decrease in the tensile strength of the polyester, and as more dye is taken up, an increase in tensile strength is observed. Bird et al.⁵ and Schuler and Remington⁹ have concluded that there are specific bonds between disperse dye and the PET, while Patterson⁸ strongly supports specific bonding between PET and disperse dyes and suggests that the dye molecules are located in the amorphous regions of the polymer. The location of the dye molecules in the amorphous regions depicts some initial resistance in dye uptake by the crystalline regions.

TABLE II
Properties of Disperse-Dyed PET Fiber

Dyeing time, min	% Dye absorbed $\times 10^{-2}$	Specific stress, g/tex	Extension at break, %	Initial modulus, g/tex	Secant modulus at break, g/tex
4	blank dyed	8.0	30.0	21	0.26
144		8.3	26.0	22	0.37
4	2.0	5.5	16.7	27.0	0.33
16	4.5	6.0	16.7	27.5	0.35
36	6.5	6.5	13.3	25.0	0.49
64	10.0	7.5	13.3	30.0	0.56
100	22.0	8.6	10.0	35.0	0.86
144	23.0	8.6	10.0	37.5	0.86

The combined effect of heat, time, and the accompanied specific bonding effect of the dyes would culminate in the reduction of the "effective" amorphous region and possibly an enhancement in the crystallinity of the polymer. The observed increase in specific stress values for fibers dyed for 100 min and more compared to the blank dyed fibers lend some support to this view.

However, further work is in progress to determine the extent of this possible enhancement in the crystallinity of the fiber and data on x-ray diffraction and DSC-2 measurements should prove useful.

During the dyeing there was more than enough dye to saturate the dye bath. Under the conditions used, the dyeing can be said to be carried out in an "infinite" dye bath in which the dye concentration does not change. It must be emphasized that at 100°C the chain segments in PET have a relatively high freedom of movement and the dye molecules will easily penetrate the polymer, whereas at lower temperature, for example 80°C, the polymer is almost in the glass transition region and molecular motion is much more difficult. From Table II it would be possible to calculate the diffusivity of the dye, since when the sample is not near dye saturation a linear relation between percentage dye on the fiber and the square root of the dyeing time can be shown to exist.

The mechanical parameters that more clearly illustrate the effect of dyes and dyeing on polymer behavior are the percent extension at break and initial modulus. The percent extension at break of the PET fibers decreases on dyeing, and as more dye is absorbed a further decrease in the parameter is observed. Conversely, disperse dyes have the effect of increasing the tensile stiffness or initial modulus of PET fibers as shown in Table II.

CONCLUSIONS

Interest in the possibility of attaching dyes to fibers by chemical reaction giving rise to covalent linkages between dye and fiber arose from the supposition that high wet fastness would result from uniting the dye and the fiber to form a single molecule. The stability of such a molecule must depend upon the resistance of the covalent linkage to reagents, and this will vary with the nature of the link itself. Some difficulty is therefore encountered in extracting dyes from reactive-dyed cotton due to the strong bonding between the fiber and the dye. Extraction of disperse-dyed PET is relatively easier. However, the effect of reactive

and disperse dyes and dyeing on the mechanical properties of cotton and PET are reflected in gross changes in such parameters as specific stress, extensibility, and initial modulus.

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Received June 4, 1979

Revised October 29, 1979