

# Changes in Surface Properties and Dyeability of Polyethylene Terephthalate Fibre Pretreated with Selected Chlorinated Solvents

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**Abstract** Scanning electron microscopy (SEM) and X-ray diffractometry (XRD) analyses has been used to investigate the structure of polyester fibre surface before and after treatment in some chlorinated solvents; perchloroethylene (PCE), trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE) and tetrachloromethane (TCM) for different times in relaxed condition at room temperature. The results of the scanning electron micrographs did not show any observable internal damage in the fiber structure. On the surface however, several changes such as presence of micro voids, roughness and scissions of varying shapes, magnitudes and spacing density have been observed. The intensity of the diffracted peaks from the X-ray diffractographs of the treated fibre also showed a fall compared to the control one which may be accounted for in terms of the surface structural changes earlier on observed. The pretreatment of the polyester fibre with the chlorinated solvents was found to improve the dye uptake of all the treated fibres in the order of TCE > 1,1-DCE > PCE > TCM; this may be due to the large increase in the inter surface area swelling and greater segmental mobility of polymer molecules. TCE was found to be the best among the four solvents in terms of improvement in dye uptake. The improvement in the fastness properties (wash and light) of the pretreated fabrics was also observed. The chlorinated solvents used in this experiment caused structural differences on surface structures of the polyester fibres and these changes are very crucial to the behaviour of the polymer in fibre processing for other essential usage.

**Keywords:** SEM, XRD, polyester, scission, dyeing, chlorinated solvents, fastness

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## 1. Introduction

Commercially important polyester such as polyethylene terephthalate, commonly referred to as PET is gaining popularity as one of the most versatile engineering polymers due to its high strength and excellent mechanical properties. Therefore, its applications have been extended to many areas including textile industries, microelectronics and solid state devices (Bhat and Naik, 1984 and Bal and Behera, 2006).

Chemical treatment of PET with different solvents brings about change in the fine structure and improvement in some important properties like dyeability and wettability of polymers (Hsieh *et al.*, 1996). The chemical energy which causes the disruption of the intermolecular cohesive forces between the chains is assumed to be generated by molecular interaction between polyester fibre and the solvents leading to the formation of solvated bonding sites within the polymer structure and this forms a major difference between thermal and solvent-induced shrinkage of PET.

Several methods has been highlighted for modifying polyesters using solvents but in recent times plasma method is adopted to improve dyeability in which the fiber has to be treated with acids and alkali before exposure to plasma (Bal and Behera, 2006 and Arun, 1999). Treating polyester fibres with suitable solvents is expected to give useful morphological structure to the polyester.

Scanning electronic microscope (SEM) has been used to probe the structure of the polyester fibres upper layer while X-ray diffraction (XRD) studies on a polymer are mainly concerned with study of crystalline, amorphous and semi crystalline regions that are responsible for observing their respective electrical and mechanical properties. X-ray diffraction patterns of most polymers contain sharp as well as broad and diffuse peaks. The sharp peak corresponds to crystalline regions; the diffuse and the broad ones refer to amorphous.

Jameel *et al.*, (1982) studied the effect of orientation on the surface morphology of PET resulting from the solvent treatment over a wide range of temperatures and reported that with increase in orientation, the solvent treatment causes less and eventually no modification in the surface texture. Ito *et al.*, (1992) studied the surface morphology

of PET fibres treated with DMF/Water mixture using SEM technique and observed that the fibres treated with solvent containing mixture of lower water fractions showed a significant surface roughening which increases on decreasing fraction of water. The surface roughening is said to be due to the partial dissolution of the PET surface and not to the molecular degradation. Muralidharan and Laya, (2011) studied the surface topography of PET fibres using scanning electron microscopy (SEM) and noted that azeotropic mixtures attacked almost the entire surface of the fibre and caused erosion.

PET fibres are hydrophobic with a compact structure as a result of the stiffness imparted to the chain by the phenyl residue of the terephthalate groups. PET fibres contain no basic or strongly acid groups; hence they are not generally dyeable with anionic or cationic dyestuffs. Dyeing of polyester fibre with disperse dye has always been carried out using high temperature/ high pressure (HT/HP) or carrier assistants. An alternative approach to achieve dyeing process at nearly atmospheric pressure is to modify the structure using organic solvents that can be recycled easily and inexpensively. Organic solvents can modify the PET fibre in a temporary way either as an addition to the dye bath (or as a major dyeing medium) or to modify the fibre structure by a pretreatment process. The rate at which a dye molecule can diffuse through a textile fibre is determined by the strength of the absorption forces between dye molecule and polymer chain and the resistance to the movement of the dye imposed by the polymer chains. In the study of the effects of fibre structure and its modification on the behaviour of PET, it is appropriate to select a dyeing temperature ( $T_d$ ) that will reveal the effects of various modifications on the dyeing properties.

The presence of such solvents within the amorphous region of the polymer is also known to depress the melting temperature,  $T_m$  of the polymer. In a predominantly amorphous polymer, the  $T_g$  i.e temperature at which substantial segmental mobility in the polymer chains becomes possible (Walters and Buchanan, 1977), may be so depressed, that the amount of mobility involved becomes sufficiently large to relax the kinetically restricted molecule of the glassy state, thus setting the polymer within the effective crystallization temperature ( $T_m - T_g$ ) domain. Usually, the  $T_g$  is lowered more than the  $T_m$  and the greater the temperature difference between the two parameters i.e  $T_m - T_g$ , the wider this crystallizable temperature range is, the greater will be the degree of crystallinity that is achieved (Johnson and Popoola, 1991).

The present authors had carried out some investigations on the effect of perchloroethylene (PCE), trichloroethylene (TCE), 1,1 dichloroethylene (1,1 DCE) and tetrachloromethane (TCM) on the structural behaviour of the treated PET using XRD and SEM techniques. Noting the above work and the usefulness of modified fibres in view, the present investigation has been undertaken to study the effect of chlorinated solvents treatment on the surface property changes (SPC) and dyeability of polyethylene terephthalate fibre.

## 2. Materials and Methods

The pretreatment was carried out using the method of Johnson and Popoola, (1991) where the fibre was purified

from spin finish by extracting with petroleum ether at 60°C for 1 h followed by scouring at 60°C in aqueous solution of Lissapol (non-ionic surfactant), washing and then drying under vacuum at 60°C for a further period of 24 hr prior to use for liquid treatment studies. The purified PET fibres weighing approximately between 30-50 mg each were subsequently treated in the selected chlorinated solvents (PCE, TCE, 1,1-DCE, TCM) at room temperature in a 2 L culture flask for varying times for liquid-induced crystallinity in relaxed condition. At the end of each treatment time, they were removed and blotted dry of surface – held liquid, pressed under standard load (200g) to ensure complete removal of unabsorbed liquids, air-dried and further dried in a desiccator containing silica gel also for a period of 24 hr (Popoola, 1993).

### 2.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy studies were made on treated and control samples with S-3000H- Hitachi, (Japan made machine) to study surface modifications (if any) caused by the chlorinated solvents. The samples were imaged at different magnifications (X200 and X500) for better understanding of the inner core of the sample.

### 2.2. X-RAY Diffraction (XRD) Studies

X-ray diffraction studies using PAnalytical-mode X'pert PRO was carried out for both control and solvent treated PET fibres to determine the crystalline and amorphous region of both the treated and control samples. The samples were analyzed by observing number of counts as a function of scattering angle ( $2\theta$ ).

### 2.3. Dyeing of Treated and Untreated PET Fibres

Disperse blue 1 dyestuff was purified by extraction with acetone followed by successive recrystallization in distilled toluene. The pure grains were dried under vacuum in an oven at 60°C, ground into a fine powder to enhance dispersibility. Dye solutions of varying concentrations were prepared and their absorbances determined at the wavelength of 607 nm for which it was found to show maximum absorbance and the validity of Beer-Lambert law established by a linear correlation between the dye concentration and the optical density. The dyeing of control and solvent treated PET fibres in purified disperse dyestuff was carried out for each of the samples using Roaches (MB model) dyeing machine in succession using different dyebaths at a dyeing temperature ( $T_d$ ) of 80°C for 1 hr without the use of any carrier at a liquor ratio of 100:1. After the dyeing, the dyed fibres were taken out, rinsed in hot and in cool water and later air-dried at room temperature.

### 2.4. Measurement of Dye Uptake

Spectrophotometric method was used for the measurement of the dye absorbed by the solvent treated and control PET fibres using spectrometer 721 (2000 model). The optical densities of the initial dyebath before dyeing and the residual liquor after dyeing were measured at 607 nm. From the optical density obtained, the concentration of the residual liquor was determined from

the standard curve obtained earlier. The difference in the concentration of dye in the dye liquor before and after dyeing was determined from the standard curve and hence the amount of dye uptake (mg/g) was calculated.

### 2.5. Fastness to Washing

The dyed samples were subjected to washing in an International Standard Organization (ISO) washing fastness condition. This is to determine the dye-fibre bond stability. A liquor ratio of 50:1 was prepared at 2g/l soap solution at 60°C for 45mins. Equal weight of the control sample was added to determine the degree of staining. After the washing, the samples were rinsed thoroughly, dried and assessed using the Gray Scale for change in shade and degree of staining.

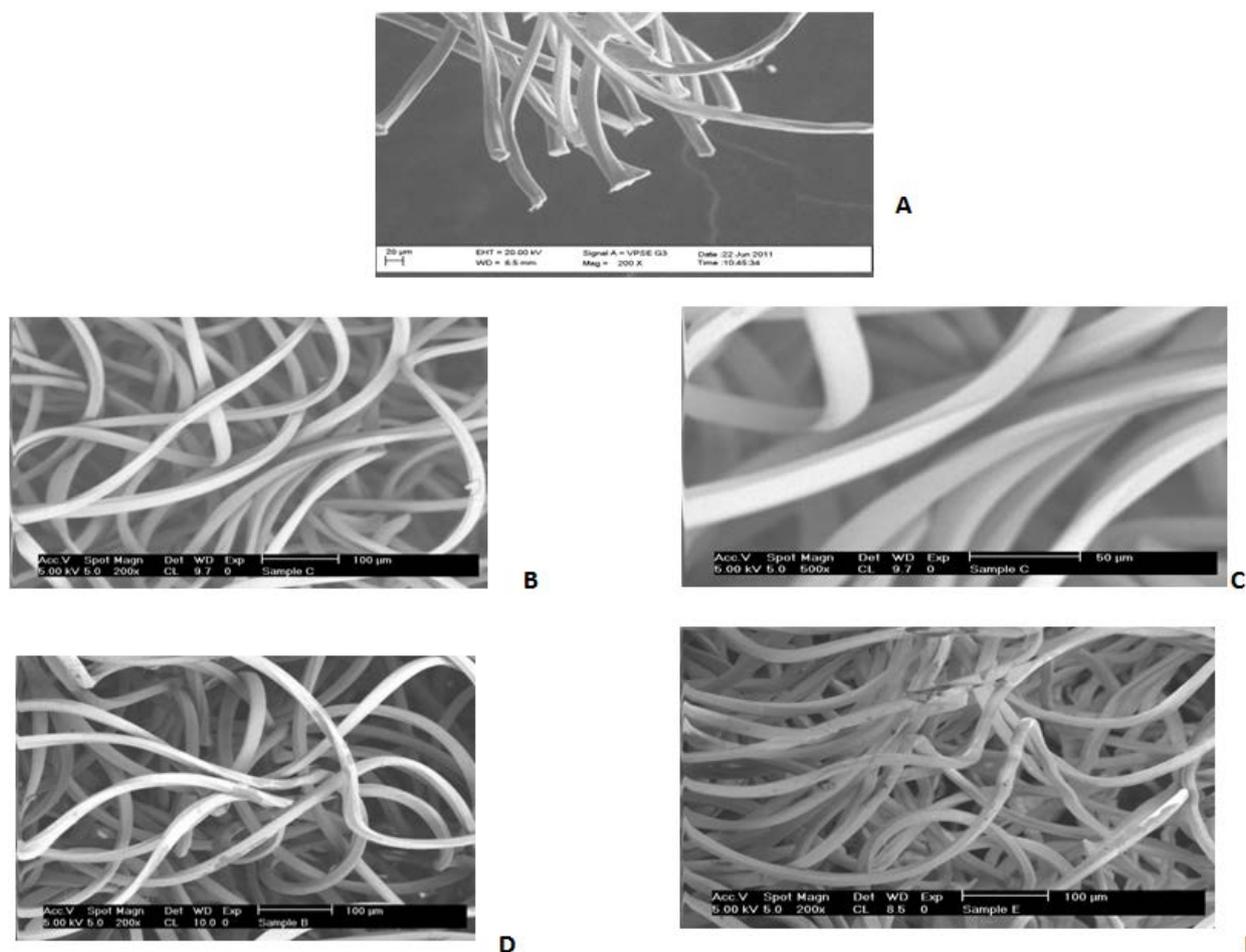
### 2.6. Fastness to Light

The already dyed samples (from the pretreated and control samples) were mounted on black board paper. The mountants were then exposed to artificial light for approximately 84 h in the laboratory. At every 12 h, the mountants were checked using light fastness tester to see if any of the dyed samples and Blue standards has faded comparably in the same way. Changes noticed on the treated samples and that of the Blue Standard were rated similarly on a blue scale. A similar test procedure was carried out for the control sample as a means of comparison.

## 3. Results and Discussion

The fibre surface was analyzed in order to follow the surface changes and physical properties of the fibre during the course of the solvent treatment by comparing the micrographs of polyester fibres from different treatments and the control fibre. The surface of the polyester fibres modified by the solvents had unique characteristics as shown by the SEM. These appearances reflect the different degrees of solvent modification of the untreated polyester surface corresponding to the different interacting efficiency of the solvents. The following characteristics were noticed in the analysis of the control and 900 secs (chlorinated solvents) treated fibres at X200 magnification as shown on plate 1 below. From the plate, the control fibre has relatively smooth surface texture and microscopic appearance. TCM and PCE treated fibres has little bit of roughness or damage observed on the fibre surface and no decrease or increase in the fibre diameter compared to the control was noticed, 1,1- DCE and TCE treated fibres attacked the entire surface of the fibre, more roughness and softness of fibre surface was noticed while the presence of micro voids becomes more apparent on the fibre surface. With the TCE treated fibre however, differentiation and scission becomes more apparent on the fibre surface with reduction in the fibre diameter as a result of high rate of oligomer loss.

### 3.1. Results



**Plate 1.** Scanning Electron Micrographs of Control (A) and 900 secs Treated PET fibre in PCE (B), TCM (C), 1,1-DCE (D) and TCE (E) at 200X Magnifications

Summarily, all the treated fibres showed more surface roughening (especially with 1,1-DCE and TCE) than the control fibre, which may be due, to the partial dissolution of the PET at the surface and not to degradation. The porous structure produced on the fibre surface by these treatments is a basic requirement for the penetration of dyes into the fibre. It also assists in higher wettability and better wears properties of the textile material. The

observed results of surface roughening and formation of cracks resembles those of earlier reports available (Jameel *et al.*, 1982, Rajendran *et al.*, 1996, Wafaa *et al.*, 2010 and Chidambaram *et al.*, 2003).

XRD patterns were recorded for the control and treated PET fibres to evaluate the effects of the four chlorinated solvents on the PET fibres as shown on Figure 1.

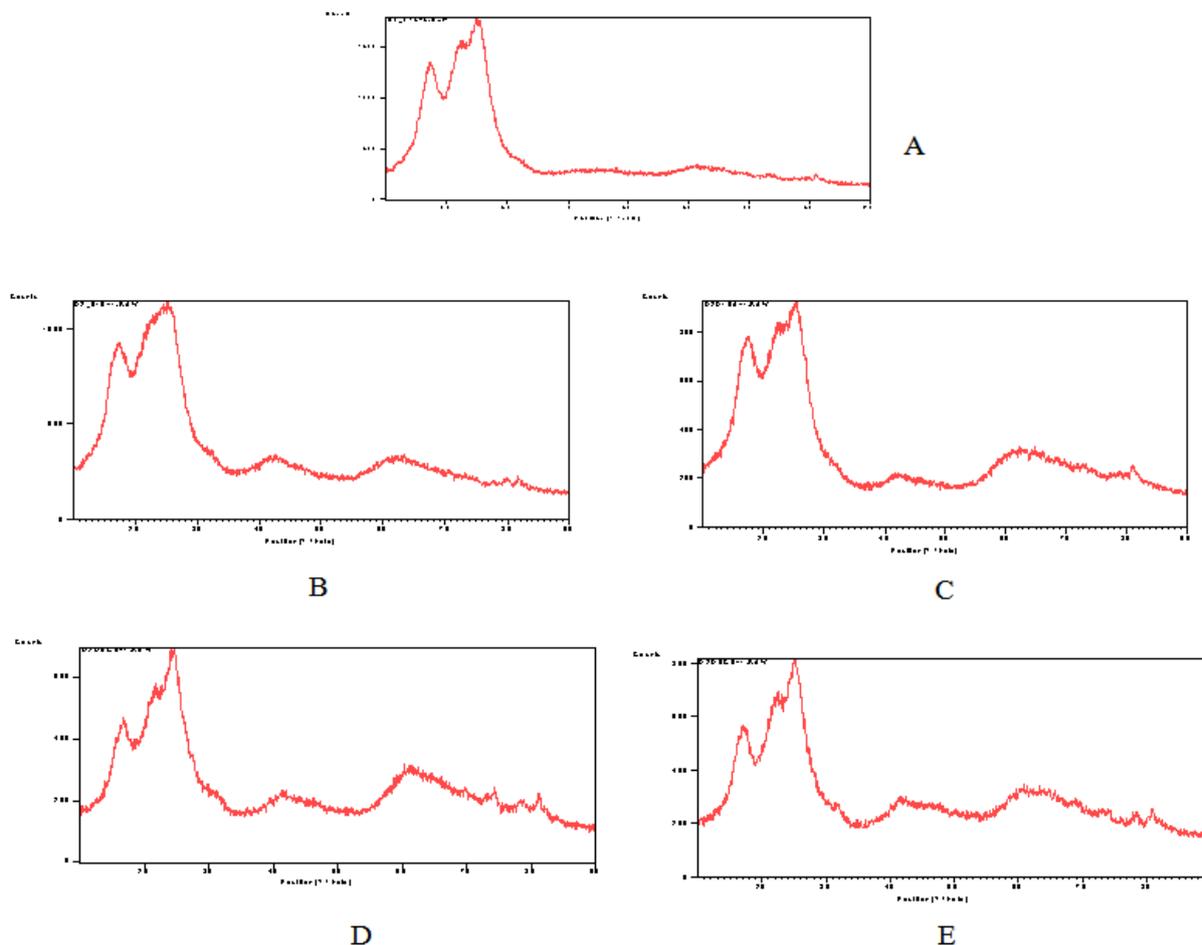


Figure 1. X-Ray Diffractograms of Control (A) and 60 secs solvent treated fibres in PCE (B), TCE (C), 1,1 DCE (D) and TCM (E)

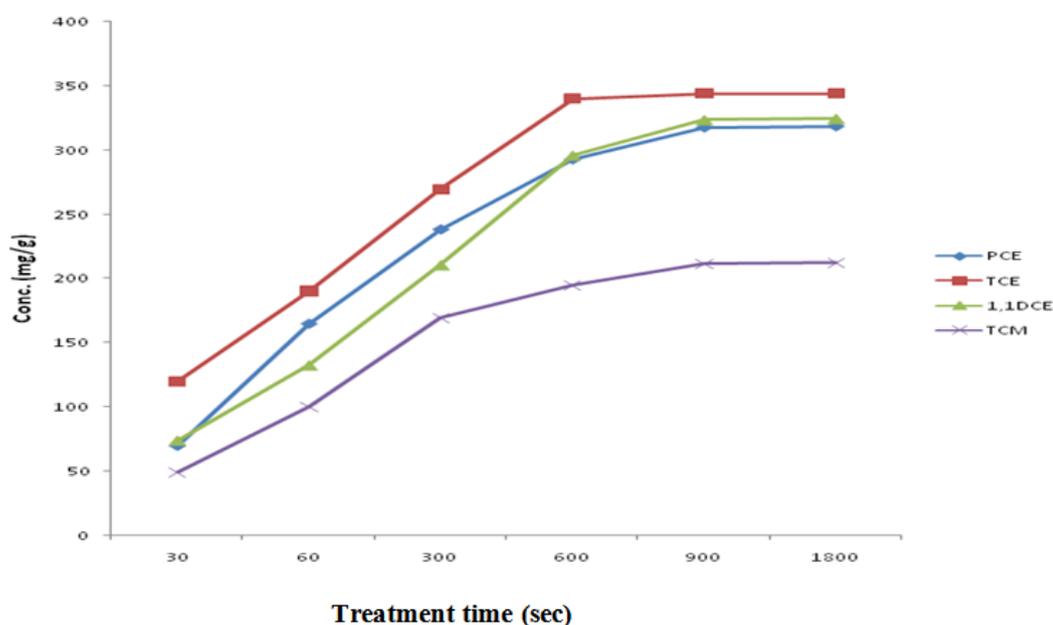


Figure 2. Dye Uptake of the Treated PET Fibres in Aqueous Solution of Disperse Blue 1 (Note: Control fibre dye at 80°C for 1 hr is 33.3 mg/g)

The diffractographs for the control showed the highest count (relative intensity) of above 1500 at 2 $\theta$ . This was found to decrease in all the treated fibres, which is an indication of increase in the amorphous percentile of the treated fibre over the control sample. The change in the position of the peaks shows that the solvent treatments have affected the crystallinity of the PET fibres because of their solubility within the polymer and the interaction efficiency of the liquids, especially for fibres at shorter treatment time. This observation depends relatively on the amount of the different liquids retained within the polymer and the interaction of the solvents with polymer is expected to result in possible recrystallization and decrystallization of the corresponding polymer contents.

The effect of solvent pretreatment on the dyeing behaviour of the PET fibres was studied by dyeing the pretreated and control fibres at 80°C for 1 hr. The results are presented graphically on Figure 2. Better dye uptake was observed in all treated fibres compared to the control ones with 33.3 mg/g dye uptake at 80°C. The observed increase in dye uptake of treated fibres resembles those reported elsewhere (Muralidharan *et al.*, 2004 and Chidambaram *et al.*, 2003). The dye uptake for all the treated samples increased consistently up to 900 secs treated fibre after which equilibrium dye uptake was established. The changes in the dyeing behaviour of these treated fibres reflect changes on the fibre structure caused by each of the four chlorinated laundry solvents in terms of increase in the amount of voids or roughness created on surface of the treated fibres.

The rate at which a dye molecule can diffuse through a textile fibre is determined by two principal factors: the strength of the absorption forces between dye molecule and polymer chain and the resistance to the movement of the dye imposed by the polymer chains. The improved dye uptake of the treated fibres compared to the control fibre can be interpreted in terms of the effects of the amount of the various solvents retained within the polymer after treatment. The presence of such solvents within the amorphous region of the polymer is also known to depress the melting temperature,  $T_m$  of the polymer. In a predominantly amorphous polymer, the  $T_g$  i.e temperature at which substantial segmental mobility in the polymer chains becomes possible (Walters and Buchanan, 1977), may be so depressed, that the amount of mobility involved becomes sufficiently large to relax the kinetically restricted molecule of the glassy state, thus setting the polymer within the effective crystallization temperature ( $T_m - T_g$ ) domain. Usually, the  $T_g$  is lowered more than the  $T_m$  and the greater the temperature difference between the two parameters i.e  $T_m - T_g$ , the wider this crystallizable temperature range is, the greater will be the degree of crystallinity that is achieved (Johnson and Popoola, 1991).

As observed by the authors in the first part of the research work, 1,1-DCE was found to have the highest solvent retention value followed by TCE, PCE and the least value by TCM, the amount of solvent retained acts as plasticizer in the fibre, that breaks the intermolecular bonds, relax residual orientation and decrease glass transition temperature ( $T_g$ ). The plasticization of the fibre by three of the solvents (1,1-DCE, PCE and TCE) with respect to closeness of solubility parameter allow the chain molecule within the fibre to move past each other,

enhancing segmental mobility that leads to improved diffusion of dye molecules inside the fibre structure. From the foregoing, the degree of interaction of solvents with PET (i.e plasticization) is directly related to the extent of lowering of the  $T_g$  value. The possible few bigger size crystallites on TCM treated fibre may have caused the reduction in the accessible space on the fibre surface for the dye molecules to penetrate into the structure or act as a barrier to the dye molecule movement, thereby accounting for the low dye uptake of TCM treated fibre. The observed trend of the improvement in the dye uptake from was found to be TCE > 1,1-DCE > PCE > TCM.

The improved dye uptake behaviour of TCE treated fibre could be as a result of the fact that 1,1-DCE is a low boiling solvent (b. pt 31°C) compared to the other three solvents and is most likely to have been removed through evaporation from the fibre structure during the early phase of the dyeing and therefore not available in sufficient quantity to produce desirable effects at the dyeing temperature  $T_d$  of 80°C or due to the high rate of oligomer loss from the TCE treated fibre during treatment compared to 1,1-DCE treated fibre, that resulted in more roughening and scission that were observed from the scanning electron micrographs (SEM) with attendant increase in dye uptake.

### 3.1.1. Fastness (Wash and Light)

The changes in colour of all the treated and control polyester fibres under study due to washing are given on Table 1. From the Table, the washing fastness of all the fibres under study was found to be almost unaffected due to various solvent treatments made. These were observed to be good- excellent according to the International Standard Organization (ISO) gradings. Table 2, showed the results of light fastness for treated and control fibres. As observed for washing fastness, an improvement was also observed in the treated fibres compared to the control fibre. It is known that light fastness properties of any dyed materials depend on the stability of the dye chromophore fibre against UV radiation.

**Table 1. Wash Fastness Properties of the Treated Fibres**

Pretreatment time (sec)	Grading			
	PCE	TCE	1,1 DCE	TCM
30	3	4	3-4	3
60	3-4	4	3-4	3
300	4	3-4	4	3
600	3-4	3-4	4	3-4
900	4	4	3-4	3-4
1800	3-4	4	4	3

Untreated fibre = 2

Scale

1- Very poor or badly changed/stained.

5- Excellently unchanged or not stained.

The results of wash fastness properties of solvent treated and untreated fibres are presented in Table 1. The values obtained for the solvent treated and dyed fibres were higher compared to the untreated fibre which is an indication that the treatments has enhanced dye

penetration due to fibre swelling and hence, during washing, dye molecules cannot get out from the polymer easily. An average of 3-4 out of a grade of 5 (from Grey scale) was obtained for the solvent treated and dyed fibres. The results of light fastness properties of the solvent treated and untreated fibres investigated are presented in Table 2. Out of the grade of 8 (from Blue scale), the values obtained for the solvent treated and dyed fibres were higher than that of the untreated fibre which is due most importantly to the stability of the dye chromophore against UV radiation.

From Table 1 and Table 2, there is an improvement in the washing and light fastness properties of the treated fibres which may be as a result of the better penetration of dye into the fibre matrix due to solvent pretreatment that has created enough openings for the deposition of the dye to enhance dye-fibre bond stability.

**Table 2. Light Fastness Properties of the Treated Fibres**

Pretreatment time (sec)	Grading			
	PCE	TCE	1,1 DCE	TCM
30	4-5	4-5	5	4-5
60	5	5-6	5-6	4-5
300	5-6	5-6	6	5
600	5-6	6	7	5
900	6	7	7	5-6
1800	6	7	7	6

Untreated fibre = 4

Scale

1- Badly faded after the test.

8- Excellently maintained colour after the test.

### 3.2. Conclusion

Studies on surface topography using scanning electron microscopy (SEM) showed that the four solvents attacked the fibre surface differently. TCE and 1,1-DCE interacted strongly and attacked the surface of the polymer while PCE and TCM does not cause much damage to the fibre surface. XRD studies showed that the solvent pretreatment of polyester fibre caused reduction in the diffraction peaks, an indication of increase in amorphous region compared to the control sample. Increase in the dye uptake was observed in all the treated fibres compared to the untreated fibre. The TCE pretreated fibres gave the highest value of dye uptake which as been associated with the possibility of high amount of oligomer loss as well as greater

scissions observed on the surface of TCE treated fibres. The structural changes observed are very crucial to the behaviour of the polymer in other finishing and end use operations such as dyeing, dry cleaning, stain removal, and comfortability during use. This report therefore would be a useful guide to textile manufacturers and consumers during fibre processing and use stages.

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