THE DYEABILITY AND PROPERTIES OF STRUCTURALLY MODIFIED POLYETHYLENE TEREPHTHALATE FIBRES

By

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DEDICATED TO EME ETE AND ETE EKPO
MY DEAR PARENTS WHO HAVE
NOT WAVERED IN THEIR
GUIDANCE, CARE AND
UNFLINCHING SUPPORT.

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A B S T R A C T

The effect of solvent - treatment on the dyeability and mechanical properties of polyethylene terephthalate (PET) has been studied. The mechanical properties of the dyed PET fibres and some heat-set PET samples are also given. It was observed that strongly interacting solvents such as N,N-dimethyl formamide (DMF) and acetonitrile (CH.CN) improved the dyeability of PET which had been treated with these solvents at 74^0C for 15 minutes prior to dyeing with disperse dyes at 100 C. The relative dye-uptake after DMF-treatment is 20 times greater than after acetonitrile treatment. Pretreatment in both solvents resulted in a lowering of tensile strength. Dyeing caused a decrease in tensile strength, extensibility and initial modulus at saturation but these properties improved when that initial saturation interval was exceeded.

Solvent - treatment and heat-setting led to improvement in the crystallinity of the PET fibres. Although the densities of the various - treated PET fibres cannot be entirely relied upon due to errors caused by the use of the carbon tetrachloride - n-heptane mixture in the gradient column, the trends suggest that density increases with increase in heat-setting temperature

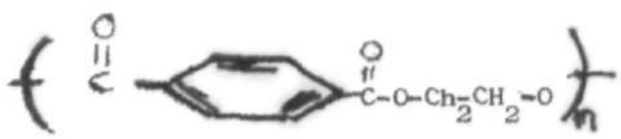
CHAPTER I

INTRODUCTION

Polyethylene terephthalate (PET) is a fibre whose principal end-use is in textile manufacture. It can be processed into fabric, either alone, or in blends with other textile materials such as cotton, rayons and wool. The fibre and fabric are marketed under several trade names, depending on the country of origin namely: Terylene (U.K.), Dacron (U.S.A.), Lavsan (U.S.S.R), Tergal (France), Terital (Italy), Diolen and Trevira (Federal Republic of Germany), Enkalen (Holland), Lanon (German Democratic Republic), Svitlen (Czechoslovakia) and Nigerlene (Nigeria).

1.1 STRUCTURE AND PROPERTIES OF PET FIBRE

As a result of the application of various methods of investigation, it is possible to represent the structure of polyethylene terephthalate in the following way:-



Polyethylene terephthalate consists of a mixture of crystalline and amorphous regions, the relative proportions of which depend on the method of preparation. The molecule has an extended rectilinear shape, the plane of the benzene rings being parallel to the (100) plane.[1] The - COO - group is out of the plane of the benzene rings by 12^{o} and the ethylene glycol residue by 20^{o}. In a stretched fibre, the axes of the molecular chains are inclined in relation to the fibre axis in such a way that the (230) plane remains vertical and the inclination of the (001) plane to the fibre axis increases. The macromolecules are linked only by Van der Waal's forces and the high melting point is due solely to the rigidity of the aromatic - nucleus - containing chain.(1) Ward(2) has shown that in crystalline polyethylene terephthalate, the ethylene glycol residue i.e. $-OCH_2\ CH_2-O-$ exists in the trans configuration.

The specific gravity of polyethylene terephthalate with a considerable amount of crystalline fraction is generally quoted as 1.38. The completely amorphous fraction obtained by rapid cooling from the melt has a specific gravity of 1.33 while the completely crystalline fraction has specific gravity 1.455. The refractive indices at $20^{o}C$ are 1.72 parallel to the axis of the fibre and 1.54 perpendicular to the axis giving a birefringence value of 0.18. The glass transition temperature (Tg) for polyethylene terephthalate lies between 80 and $90^{o}C$ and its melting point lies within the range 250 - $265^{o}C$. Being a hydrophobic fibre, polyethylene terephthalate has a moisture regain value of 0.4% at 65% relative humidity and $20^{o}C$.

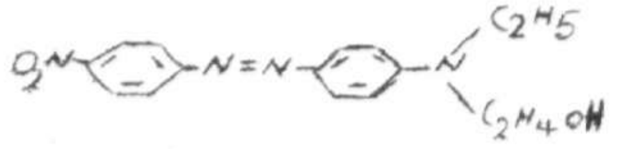
The polyester fibre is extremely stable to the action of oxidising agents such as sodium hypochlorite, hydrogen peroxide, sodium chlorite and potassium dichromate. Reducing agents such as sodium hydrosulphite do not cause loss of strength of the polyester after prolonged exposure at 80°C.

Mild acids act on the fibre more weakly than alkalis.[3] A strong solution of ammonia has a particularly powerful action. Strong sulphuric acid simultaneously dissolves and decomposes it.[4] It is also decomposed by nitric acid.

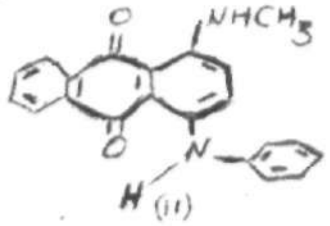
Compared to most other fibres, polyethylene terephthalate has high tensile strength and elongation - at - break per cent as well as high initial modulus of elasticity. The polyester fibre is closest to silk in its properties. It retains creases and the form imparted to it well even under damp conditions.

1.2 KINETICS AND MECHANISM OF DYEING PET FIBRE

Only dyes having a measurable affinity for polyethylene terephthalate fibres are those which can be applied from aqueous dispersions. Such dyes include disperse dyes, certain azoic dyes and in special circumstances as in the Thermosol process, Vat dyes. Typical disperse dyes have azobenzenoid (1) and anthraquinoid (11) structures shown below:-



(i)



(ii)

In use, disperse dyes are dispersed in an aqueous solution and the dye is considered to be transferred to the fibre through the solution phase, even though its aqueous solubility may be very limited. Dye in dispersion is solubilized in the micelles of the dispersing agent which form a reservoir readily available to supply more dye to maintain the strength in solution.

The rate at which the dye diffuses from the solution onto the substrate, i.e. the fibre, otherwise known as the flow rate, is controlled by the laws of convective diffusion. Near the fibre surface, a state of flux exists due to a disproportionate distribution of the dye molecules between those regions nearer to it and those farther away. The actual concentration of dye molecules in this region, known as the diffusional boundary layer, is time dependent. In a quasi-steady state, where it is assumed that the number of dye molecules leaving the layer is equal to those arriving and that any dye molecule that comes into contact with the surface is immediately adsorbed, the complex mathematical equations attendant on the original problem yield themselves to easier solutions through the application of Fick's laws of diffusion.

For an idealized plane sheet having the dimensions shown in Fig. 1., Macgregor and Peters[5] have obtained the diffusion coefficients by solving the relevant differential equations, subject to appropriate boundary conditions. The relevant equations are:-

$$J_s = -D_s \left(\frac{C^1 - C}{\delta_D} \right) \text{ .... (i)}$$

$$\frac{\partial c}{\partial t} = D_f \frac{\partial^2 C}{\partial x^2} \text{ .... (ii)}$$

where J_s = quantity of flux within the diffusional boundary layer.

D_s = diffusion coefficient within the diffusional boundary layer.

C^1 = steady-state concentration within the diffusional boundary layer.

C = the solution concentration.

δ_D = the thickness of the diffusional boundary layer.

C = the concentration of dye at time, t, at a point, x, such that $-\ell < x < \ell$ in the sheet.

D_f = the diffusion coefficient in the polymer sheet.

Mathematical solutions to the convective diffusion problem increase in difficulty when the sheet or film is replaced by a rod or groups of rods as would be used to represent a fibre or bundles of fibres. In addition, when the boundary condition, C = 0, is removed and concentration at the surface becomes, as it must in a real dyeing system, a function of time, the compli-

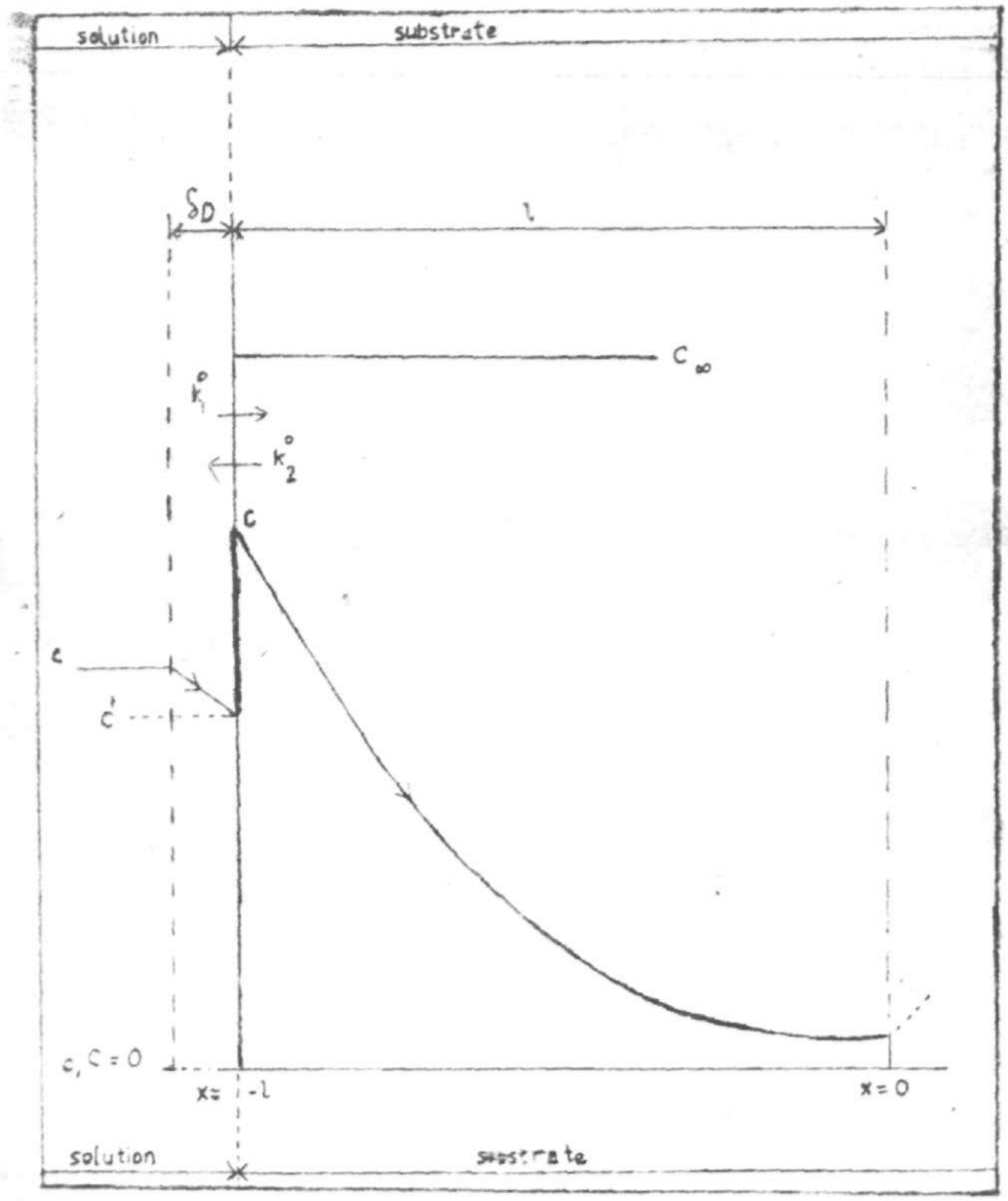


Figure 1: Diffusional Boundary Layer for a plane sheet of thickness 2l
$\overset{\circ}{k}_1$, $\overset{\circ}{k}_2$ ≡ dye velocity constants for passage in and out of subststrate respectively
(after Macgregor and Peters)

cations increased and the problem is yet to be resolved. The rate of dye uptake in any system, sheet or cylinder, has been shown[(5)] to depend on the values which may be attributed to a parameter L represented as:

$$L = \frac{D_s \, l}{K \, D_f \, \delta_D}$$

(where K = partition coefficient = $\frac{K_1^o}{K_2^o}$

and K_1^o, K_2^o, have meanings as indicated in Fig. 1.)

The effect of flow rate on rate of dyeing can be expressed quantitatively by its effect on the thickness, δ_D, of the diffusional boundary layer; increases in flow decrease δ_D and hence increase L. When the flow rate becomes very high, $\delta_D \longrightarrow 0$ and hence $L \longrightarrow \infty$. At this juncture, the rate of dyeing is now controlled by the rate of diffusion within the solid and further changes in stirring have no effect on the rate of dyeing. In effect, this means that in a well - stirred dyebath, the rate - determining step in the kinetics of dyeing is diffusion through the polymer matrix.

Marsden and Urquhart[(6)] demonstrated that simple non-ionic proton donors, e.g. phenol, when present even at low concentrations, were readily adsorbed by cellulose acetate. They suggested that this was due to the occurence of hydrogen bonding and proposed the theory of adsorption by site bonding. Vickerstaff[(7)]

later extended this concept to dyeing with disperse dyes, all of which contain simple polar groups in their structure. Most disperse dyes contain proton donor groups eg. -OH, or $-NH_2$ as well as proton acceptors e.g. C=O, -N=N-, $-N(CH_3)_2$ and $-OCH_3$. Hydrogen or other types of bonding is possible between these groups and those of opposite polarity in the polymer structure. The formation of a Π - type hydrogen bond between the aromatic nucleus of the polyethylene terephthalate and a hydroxyl group in the disperse dye molecule is also thought to play some role.

Several other workers have independently confirmed the site adsorption theory of Marsden and Urquhart. The rival theory which held that the dye molecules impart their colour to the material by a process of solid solution and propagated by a school of thought led by Kartaschoff(8) was finally discarded.

Bird et al,(9) Stubbs,(10) and White(11) showed that disperse dye adsorption did not correspond to the Langmuir model and thus advanced the case for the occurrence of site adsorption.

The main requirement for a site adsorption model to operate is that the interaction energy between the molecules in the dye crystal and in the polymer should not differ greatly from that between adsorbed dye molecules and the polymer. This enables dye and polymer to be mixed without any great change in the potential energy of the system. Marjury,(12) Patterson and Sheldon,(13) and Bird and Harris(14) have carried out experimental verification of the above requirement. Their results indicate a strong correlation between the heat of solution of dye and the heat of dyeing. Their conclusions also confirmed the theory that adsorption occurs by site occupation.

1.3 INFLUENCE OF FIBRE STRUCTURE ON DYEABILITY OF POLYETHYLENE TEREPHTHALATE.

The degree of crystallinity, or the volume fraction of the ordered regions or units within the fibre is an important characteristic of a particular polymeric material. It affects the dyeability, maximum draw ratio and many other properties of man - made fibres. Dumbleton and Murayama[15] have shown that the glass transition temparature, Tg, of polyethylene terephthalate is a linear function of the quantity $\frac{(X^1)}{(V^1)}$

(where X^1 is the total amount of crystallinity and V^1 is the average volume of a crystallite).

The rate of dyeing depends on the existence of a sufficient number of holes between the polymer chains which are large enough to accomodate dye molecules. It has been shown that a direct relationship exists between the available number of holes, i.e. the free volume, and the Tg.[16] This relationship can be expressed mathematically as follows:-

$$V_f\ (T) = V_{f,g} + \alpha\ (T - Tg)$$

where V_f (T) is the free volume at a given temperature, T.

$V_{f,g}$ is the free volume at the glass transition temperature

and α, the bulk thermal expansion coefficient.

Fox and Flory[17] have also shown that for most polymeric materials, the following equation gives a good approximation:

$$V_{f,g} = 0.025\ V_t$$

where V_t is the total volume of the polymer.

Macgregor and Peters[18] have suggested that the rate of diffusion of disperse dyes through the fibre is a direct function of the difference (T-Tg), where T is the dyeing temperature. Consequently the ratio $(\frac{X^1}{V^1})$ by influencing Tg will also affect the diffusion coefficient of disperse dyes through the fibre. Dumbleton et al[19] measured the effect of annealing temperature on both Df and $(\frac{X^1}{V^1})$ in drawn polyester fibres and found that the dye diffusion coefficients were lower in the highly drawn samples which exhibited high degrees of crystallinity. Both the temperature and draw ratio were also found to affect the value of X^1 and of V^1 but to different degrees. They, however, found that the average crystallite size became less owing to the effect of drawing on the kinetics of crystallisation. In order to explain these observations, they developed a model of dye diffusion based on morphological considerations. They postulated that many small crystallites in the fibre are more effective in restraining dye diffusion, than are a few large crystallites.

Warwicker[20] has recently reported that polyethylene terephthalate absorbs more dye when it is kept under tension in the dyebath, than when it is in the free condition. He explained that when under tension, the orientation of the fibre will be relatively higher than when it is free. This implies that some factors, other than amorphous content and amorphons orientation may be important in dye uptake. Warwicker postulated that under tension the path of dye diffusion is less tortuous and therefore more dye can diffuse into the fibre within a fixed time. The additional factor which must be considered was shown to be the morphology of the sample.

It is noteworthy that the concept of tortuosity proposed by Warwicker[20] agrees well with the physical concept implicit in the model of Dumbleton and Coworkers.[19].

A wide range of experiments performed by Weisz and Zollinger[21] gave diffusion coefficients for disperse dyes in hydrophobic fibres. The magnitude of these coefficients implied that diffusion in such fibres resembles diffusion in a liquid. Hence they deduced that dye molecules penetrate into the inner volume of the fibre through water - filled microvoids.

1.4 EFFECT OF MODIFICATION OF FIBRE STRUCTURE ON DYEABILITY OF POLETHYLENE TEREPHTHALATE FIBRES.

The diffusion of dye into individual fibres and the eventual extent of dye absorption depend largely on the physics and chemistry of the fibre structure. It has been shown that it is extremely difficult to correlate modifications in fibre structure with modifications in dyeing properties[18]. The influence of the chemical structure and the physical arrangement of the macromolecules of the fibre on the dyeing process cannot be specified with any degree of certainty. In addition, parameters of the actual dyeing process, particularly pH, ionic strength and temperature, all exert an effect.

As already noted in section 1.2, dye - fibre specific bonds are known to exist and are believed to hold the dye molecule onto the fibre. In order to penetrate deeper, the dyestuff molecule must leave the first linkage site and proceed to another. The speed at which this migration can occur will depend, on the one hand, on the strength of the dye-fibre bond and, on the other hand, on the size of the dye molecule. In practice, this problem can be overcome by either dyeing at high temperature, thereby enhancing the kinetic energy of the dye molecules or by applying dyeing aids or carriers at lower temperatures. It is believed that carriers act to counteract steric hindrance to dye mobility by causing increased chain segmental motion or a decrease in Tg of the fibre.[22]

There are two main methods of effecting modification in the fibre structure namely:

(1) heat treatment

(2) solvent treatment

Heat treatment methods encompass a broad field of fibre modification techniques, the simplest of which is heat-setting. During heat - setting, the drawn fibre is heated to a temperature higher than its glass transition temperature. The weaker inter-molecular bonds are broken and the released segments of the molecular chains will tend to move to positions which are more favourable for the formation of new intermolecular bonds of higher stability. This process is usually accompanied by axial shrinkage which becomes larger as setting temperature increases. The refolding of chains is believed to be one of the retractive forces giving rise to shrinkage. A schematic representation of possible occurrences during heat-setting is shown in Fig. 2.

Marvin[23] has shown that dye uptake relates in a complicated manner to the setting temperature of polyethylene terephthalate fibres. There was an initial decrease in dye uptake reaching a minimum at about 180^{o}C after which a progressive rise was noticed. It has been shown that this phenomenon also occurred in the dye uptake behaviour of textured polyethylene terephthalate yarns[24].

While the effects of the various heat treatment methods on dyeability have been extensively investigated and documented by several authors, the dyeability of solvent - treated polyethylene terephthalate fibres and yarns remains a relatively virgin field of research.

As stated earlier, a reduction in the Tg of polyethylene terephthalate fibres is responsible for an improvement in their dyeability. Carrier-assisted dyeing is designed to exploit this fact. Despite earlier controversy on the mechanism of carrier-

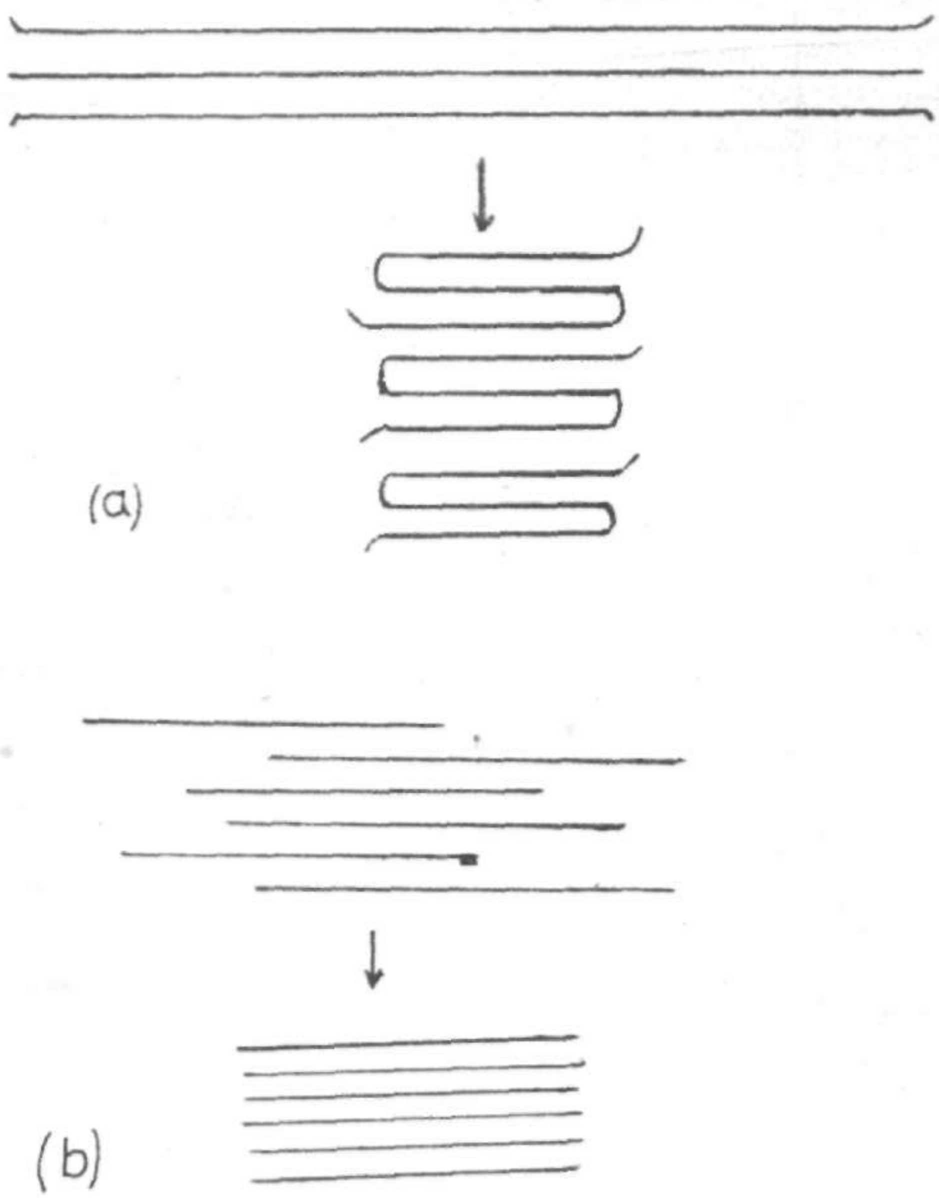


Figure 2: Length changes that may occur during heat-setting

(after Morton and Hearle)

action, Rochas[25] has after much experimental work, attributed the origin of carrier activity to the presence of some residual carrier molecules in the fibre matrix leading to some permanent physical modification in the fibre structure. More recently, Brown and Peters[26] have demonstrated that although some change in the X-ray photograph of polyester fibres could be observed when trichlorobenzene was used as the carrier, the concentration of carrier required to produce carrier activity was lower than the concentration needed to produce permanent modification of fibre structure. The plasticising ability of carriers which determines their effectiveness is, no doubt, due to a solubilizing action of some sort, which is accompanied by swelling[27]. Waters[28] has adduced evidence to prove that this is, however, not the prime criterion for carrier efficiency.

In practice, the use of carriers to achieve fibre modification is objectionable on the following grounds:-

(a) The extra cost can be considerable.

(b) The goods are inclined to retain the colour of the carriers and need very thorough washing to remove it.

(c) The light fastness of the dyeing is badly impaired by the use of some carriers e.g. p-phenyl-phenol, O-phenyl-phenol and salicylic acid.

However, studies[29] have shown that the pretreatment of polyethylene terephthalate yarns with certain strongly interacting solvents such as N, N-dimethyl-formamide (DMF), tetrachloroethane and γ - butyrolactone can lead not only to swelling but also to irreversible modidication of the fibre structure. In the case of DMF, dynamic modulus measurements confirmed that the glass transition temperature was drastically reduced from 110°C to 10°C[30]. The modified polyethylene terephthalate structure should therefore permit rapid diffusion of disperse dyes under atmospheric conditions without either the addition of carriers or use of pressure dyeing techniques. The basis of structural modification during the DMF treatment of polyethylene terephthalate yarns is solvent - induced crystallization which occurs while the polyethylene terephthalate structure is swollen with the solvent. At low temperatures only small crystallites are formed and after removal of the solvent, the swollen structure which cannot now be supported by the small crystallites consequently collapses. When DMF treatment is carried out at higher temperatures, formation of larger crystallites occur which are more stable and capable of supporting the swollen structure, so that total collapse is prevented upon the removal of the solvent.

This view has been upheld in studies with other solvents. Kolb and Izard[31] had shown that the crystallization temperature of polyethylene terephthalate was not constant but depended on the immersion media. In silicone oil, the minimum crystallization temperature was between 95.4° and 99.3°. In water, this temperature had been lowered to 70.7° - 75.6°C. Other more active media such as acetone, benzene, nitromethane and nitric acid initiated crystallization at room temperature. The lowering of the crystallization temperature had been attributed to swelling action with the media acting as weak solvent.

Solvent - fibre interaction and swelling are closely related to the soubility of a polymer in a particular solvent. In section 1.3, an allusion was made to the role played by the availability of holes or free volume in enhancing dye diffusion within the fibre. It was also shown that the free volume constitutes a fraction of the total volume of polymer. A general theory on the nature of free volume has the following as its main postulates:

(i) The free volume is allowed complete freedom of distribution so as to maintain a state of minimum free energy.

(ii) In any system, the density in a small element of volume is a constant only in the sense of a time average. It is subject to continual fluctuations having a distribution in time which is governed by well-established fluctuation theory.

(iii) A momentary decrease in the density in a volume element is accompanied by a momentary increase in its free volume and so the distribution of free volume is also governmed by the theory of fluctuations.

Bueche[32] thus developed a theory for predicting the probability of hole formation based on statistical mechanics.

Based on this theory, the number of holes, n_b, larger than the critical volume V* is given by:

$$n_b = \frac{\int_{b^*}^{\infty} \exp(-4\pi\sigma b^2/kT)\,db}{\int_0^{\infty} \exp(-4\pi\sigma b^2/kT)\,db}$$

where σ = the specific surface energy of the polymer

b = the radius of the hole

b* = the radius of the hole with volume V*.

It may therefore be concluded that the problem of solvent - fibre interaction and its attendant swelling, can be analysed from the point of view of statistical thermodynamics. In this way, swelling can be likened to solution in that there is a random interchange of position between fibre molecules and solvent molecules, but in swelling this occurs only to a limited extent, whereas in solution it continues until there is a uniform mixture of the two substances.

The free energy of mixing a solvent and a polymer is given by the thermodynamic relation:

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

Since the entropy of mixing ΔS_m is always positive due to an increase in disorder caused by the random mixing of polymer and solvent molecules, the free energy, ΔG_m, will be positive or negative depending on the magnitude of the heat of mixing, ΔH_m. Swelling or solution will be enhanced if the heat of mixing, ΔH_m, assumes a small or zero value, as this implies that the free energy of mixing will be large and negative. However, it is commonly acknowledged that most polymer solutions do not obey Raoult's laws and hence the condition that DH_m be close to zero is hardly realized in practice;

Further consideration of the nature of the forces acting between solvent molecules and those acting within polymer chains led Hildebrand[33] to the conclusion that if the internal pressures in the solvent and polymer were similar, then the heat of mixing will approach a zero value. Hildebrand defined internal pressure as the quantity represented by: $\left(\frac{\Delta E}{V}\right)$

where ΔE = energy of vapourisation

V = the molar volume

The ratio $\frac{\Delta E}{V}$ is also known as the cohesive energy density.

Finally Hildebrand formulated the following equation which has proved most useful in predicting the affinity of a solvent for a polymer:

$$DH_m = V_m \left[\left(\frac{\Delta E_1}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2}{V_2}\right)^{1/2} \right]^2 \phi_1 \phi_2$$

$$= V_m \left[\delta_1 - \delta_2 \right]^2 \phi_1 \phi_2$$

where ΔH_m = heat of mixing

V_m = total volume of mixing

ΔE = energy of vapourisation of components 1 and 2.

V = molar volume of components 1 and 2.

ϕ = volume fraction of components 1 and 2 in the mixture.

$\delta = \left(\frac{DE}{V}\right)^{1/2}$ = solubility parameter of components 1 and 2.

From the above equation when $\delta_1 \rightarrow \delta_2$, $\Delta H_m \longrightarrow 0$. Therefore, a solvent may be regarded as a "good" solvent for swelling or dissolving a polymer, if their solubility parameters have comparable values, otherwise, it may be regarded as a "poor" solvent.

The Hildebrand equation has, however, been experimentally verified only for amorphous polymers and certain solvents where there are no strong intermolecular forces interacting between the two components.[34]

1.5 SCOPE OF THE PRESENT INVESTIGATION

In the present investigation, our main purpose is to relate the effect of treatment of drawn polyethylene terephthalate fibre with strongly interacting solvents such as DMF and Acetonitrile to the dyeability of the fibres. The effect of the solvent on the mechanical propoerties of the fibres will also be studied. Comparison of the mechanical properties of solvent - treated yarns with those of a few heat - set samples will also be given.

CHAPTER II

MATERIALS AND EXPERIMENTAL METHODS

2.1 MATERIALS

(a) Polyethylene terephthalate filaments: The polyethylene terephthalate filaments used in this work were obtained from the Nigerian Chemical and Textiles Industries Limited, (NICHEMTEX), Ikorodu, Lagos. They are semi-crystalline materials having a draw ratio of 3.5 and a yarn number of 3 tex.

(b) Dyestuff: The disperse dyestuff used was Dispersol Red B - 2B.

2.2 EXPERIMENTAL METHODS

2.2.1 Purification of Dispersol Red B-2B.

2g of the disperse dye, Dispersol Red B-2B were extracted by Soxhelation. The process lasted until the filtrate coming out of the cellulose thimble was clear. The solvent used for extraction was sulfur-free toluene. The filtrate was transferred into a 25 cm^3 conical flask and concentrated to about one-third of its original volume by evaporating on a hot plate. The flask was allowed to cool to room temperature and then further cooled at $0^{o}C$ for 24 hours. The needle - like crystals formed were filtered, rinsed with distilled water and dried in the oven at $105^{o}C$ for 24 hours. The weight of dye obtained was 0.586g.

The melting point of the purified dye was $182^{\circ}C$ and its extinction coefficient, 35.67. It showed a peak of maximum absorption at a wavelength of 512 mm.

2.2.2 Solvent treatment of polyethylene terephthalate yarns

The filaments, 9.0 cm in length, were suspended in turn, from a rod placed across the top of a 50 cm measuring cylinder containing the solvent. The lower end of the yarn was loaded with a 5g weight. Since the yarn samples weighed between 0.01g and 0.05g, the force acting on the suspended samples ranged between 0.045 gf/tex and 0.009 gf/tex. The weight served to keep the filaments parallel to one another inorder to minimize entanglement. Three solvents, N,N- dimethyl formamide (DMF), acetonitrile (CH_3 CN) and methanol were used to swell the yarns. For each determination, the measuring cylinder containing the solvent was kept in a thermostatically controlled water bath.

Using methanol as the test solvent, the effect of temperature on the shrinkage property of the submaged yarns was studied. The water bath temperature was kept constant at $26^{\circ}C$, $34^{\circ}C$, $42^{\circ}C$, $51^{\circ}C$, $56^{\circ}C$ and $64^{\circ}C$ and, on each occasion, for a period of 30 minutes. The changes in length were measured in a separate experiment using the cathetometer. In companion experiments, the effect of duration of solvent treatment on the shrinkage property of the yarns was also studied using DMF and acetonitrile as the swelling media. The first sample was treated for 2 minutes while subsequent samples were treated at five - minute intervals for a period of one hour. For each solvent, the effect was studied at two constant temperatures, 42°C and 74°C. A cathetometer was also used afterwards to measure the changes in the length of the yarns.

2.2.3 Heat-setting of polyethylene terephthalate yarns

Samples of the PET weighing 4g each were exposed to dry heat without tension at 99°C, 114°C and 130°C respectively for a period of 6 hours. The experiments were carried out in a specially constructed glass apparatus. A diagram of the apparatus is shown in Fig. 5. To obtain the above mentioned temperatures three solvents: Water (B.p. 100°C), 4 - methylpentan - 2-one (B.p. 114-117°C) and Chlorobenzene (B.p. 130 - 133°C) were placed in the heating compartment, in turn, and heated to their boiling points. The vapour then rose in the column seperating the sample compartment and the stem and in the process expelled any trace of water inside the compartment and thereby causing its temperature to equilibriate with that of the sorroundings.

2.2.4 Dyeing of untreated and solvent-treated polyethylene terephthalate yarns

Two dye-baths were prepared each containing the same amount of 1g dyestuff dispersed in 1000 cm^3 of distilled water contained in a 2000 cm^3 cultureflask. One dyebath was used for the dyeing of DMF - treated yarns while the other was used for the dyeing of acetonitrile - treated yarns. About 3g each of the yarn which had previously been treated with the relevant solvent for 15 minutes at 74°C were dyed in the baths. A high, uniform, stirring speed was maintained throughout the period of dyeing. Samples were introduced into the dyeing flasks at 50°C and were removed 4, 16, 36, 64, 100 and 144 minutes after the dyeing temperature of 100°C had been attained. In addition, each dyebath contained about 0.5g of the original, untreated yarn which was dyed to maximum time. All the dyed samples were rinsed in hot and then in cold water after dyeing. They were air - dried at room temperature.

2.2.5 Quantitative determination of fixed dye on Polyethylene terephthalate fibres.

(a) Dye-extraction

The procedure of extracting disperse dyes from dyed polyethylene terephthalate fibres had previously been discribed by Erik Kissa[35]. This procedure was adopted in this experiment. 0.01g of the dyed yarn was placed in a 5cm^3 conical flask and covered with 1 cm^3 of the extraction solvent. The flask was loosely stoppered to avoid possible air oxidation of the discharged dye. The extraction solvent was DMF whose pH had previously been adjusted to 4.2 with the aid of p-toluene sulphonic acid solution in DMF. The flask was placed in a thermostatted oil-bath maintained at 140°C. The extraction time was 3 minutes. Two to three extractions were carried out depending on the concentration of the dye in the fibre. The extracts were diluted to mark with DMF in a 50 cm^3 volumetric flask. Extraction was carried out on all dyed samples.

(b) Measurement of absorbance of dye solutions

The absorbance of each dye solution was measured using the PYE UNICAM SP6 - 200 spectrophotometer which had previously been calibrated using standard dye solutions. In the very dilute concentration range, the absorbances of these solutions, when plotted against their concentrations, gave the linear plot shown in Fig. 6 in accordance with the Beer - Lambert law. From this plot, the concentrations of the dye extracts were found by interpolation. The absorbances were measured at a constant wavelength of 512 nm. The dye per cent absorbed is related to absorbance by the equation given below:-

$$\%\ \text{dye absorbed} = \frac{\text{Absorbance x extract volume x dilution x 100\%}}{\text{extinction coefficient x wt. of dyed sample x 1000}}$$

2.2.6 Measurement of mechanical properties

The mechanical properties of single polyethylene terephthalate filaments were measured on an Instron tensile testing machine, Table model 1026, with a test length of 5.0 cm in the load cell range of 50 - 500g and with cross-head and chart speed of 100 mm/min respectively. Measurements were carried out on original (untreated), solvent treated and heat-set fibre samples as well as on solvent-treated samples dyed for 4, 64 and 144 minutes.

The original (control) sample which was dyed for 144 minutes was also tested. All tests were carried out at 70% relative humidity and 22^{o}C. 5 to 7 specimens were used for each sample. The results were expressed in the form of the conventional specific stress against extension per cent graphs. From these graphs, the mean tensile strength, extension - at - break per cent, initial modulus and secant modulus - at - break were found.

2.2.7 Determination of density

The Davenport 2 - column density measuring apparatus was used to determine the densities of all the fibre samples whose mechanical properties were measured as described in section 2.2.6, except the control sample. The density gradient column was filled with a mixture of carbon tetrachloride (CCl_4) and n - heptane at 23.0 $\pm$ 0.1^{o}C. The column was previously calibrated with glass floats of known densities. Prior to suspension in the column, the fibre samples were soaked in CCl_4 for 20 hours and then allowed to equilibriate in the column for 24 hours, after which their respective heights were noted. Their densities were subsequently found from the calibration plot by interpolation.

CHAPTER III

EXPERIMENTAL RESULTS AND DISCUSSION

3.1 EFFECT OF HEAT-SETTING ON MECHANICAL PROPERTIES OF PET FIBRES

It is generally believed that stretching or drawing of polyethylene terephthalate fibres imparts a greater degree of morphological order on them. This is usually accompanied by improved crystallinity owing to a better alignment of chain molecules. Van der Waal's forces which play a major role in binding together the molecules are now rein forced by hydrogen bonds which act at closer ranges[36]. The resulting tight structure imparts strength to the fibre especially in the direction of orientation. Such a structure renders molecular penetration difficult. Hence, properties like dyeability, soil release and hydrophilicity are adversely affected. In addition, the macromolecules themselves are highly strained and are therefore in a thermodynamically unstable condition.

When drawn PET fibres are heated above the glass transition temperature, Tg, the oriented molecules in the amorphous regions will try to reach a higher entropy but their coiling is hindered by the crystalline material. With increasing temperature, the stress in the amorphous regions increases and conversely the strength of the crystalline material decreases. Hence, more and more shrinkage due to deformation of the crystalline regions occurs accompanied by a twinning of crystals or slippage of crystal planes. A new semi-crystalline molecular order emerges on freezing which is thermodynamically more stable[37].

The process described above, known as heat-setting or annealing, has considerable effect on mechanical properties. Statton et al.[38] have identified regular chain folding as the dominant morphological event occuring during heat - setting. Table 1 shows the values for the mechanical properties of the heat-set drawn polyethylene terephthalate fibres. Typical stress - strain curves are given in Figure 9. The low extensibility of the heat-set samples indicates an improvement in their crystallinity. This is confirmed by results from density determinations (Table 2.) There is also considerable improvement in mean tensile strength and initial modulus of the samples after heat-setting. However, these mechanical properties decreased with increase in heat-setting temperature while the extensibility remains constant. The decrease in tensile strength and initial modulus with increase in heat-setting temperature may probably be as a result of disorientation of the molecular structure as setting at each higher temperature creates more chain - folded sites. The increase in crystallinity with heat-setting temperature may probably be due to the fact that chain - folding places more molecular segments closer together, thereby facilitating the formation of crystallites. Plots of crystallinity - per cent against tensile strength and

TABLE 1

MECHANICAL PROPERTIES OF HEAT-SET DRAWN PET FIBRE

Measurements	PET FIBRE SAMPLES		
	Heat-set at 99°C	Heat-set at 114°C	Heat-set at 130°C
Mean Tensile Strength(gf/tex)	8.30	7.80	7.64
Mean extension-at-break %	8	8	8
Initial Modulus (gf/tex)	79.31	75	50
Secant Modulus-at-break(gf/tex)	103.8	97.5	95.5

initial modulus are given in Figures 11 and 12. They reveal an inverse relationship between crystallinity and these properties.

3.2 EFFECT OF SOLVENT TREATMENT ON SHRINKAGE OF PET FIBRES

The interaction between the polymer chains and certain solvents such as DMF and acetonitrile may provide another source of energy to cause localized disruption of intermolecular forces resulting in structural rearrangement. Compared to heat-setting technique, such solvent - induced modification has the advantage of having a lower activation energy. The action of solvent is believed to be two - fold; the disruption of intermolecular forces in the swollen state by a solubilizing action (plasticisation) and a secondary crystallization process, involving chain folding, of the newly relaxed chains[39]. Chemical annealing i.e. the action by solvents of strong plasticising ability, at room temperature is believed to be similar to thermal annealing at temperatures below 175^{o}C[39]. Structural modification caused by treatment of PET fibres in DMF at 120^{o}C for 2 minutes is of a similar magnitude as that achieved by heat-setting at 240^{o}C for 180 minutes[40]. Statton[41] has shown that increase in crystallinity due to chain-folding of relaxed chains may be related quantitatively to the observed per-cent shrinkage. The magnitude of the observed volume swelling and shrinkage depends upon the original structure (orientation and crystallinity) of the fibre and upon external variables such as temperature, time and environment. It also depends on the plasticising ability of the solvent. Knox et. al.[39] have shown that any crystallites which may be formed during treatment in a particular solvent do not affect subsequent shrinkage behaviour in stronger solvents.

In examining the kinetics of solvent - induced shrinkage, it is usually possible to identify three distinct regions along the time - axis. Plots of change-in-length per cent under various treatment conditions against time of treatment are shown in Figure 4. When they are extrapolated to the X - axis, the regions between the origin and the intercepts are known as induction periods. They represent the times required for a critical fraction of filament cross-section to be penetrated by the solvent. The second region which corresponds to the section lying along the sharper slope is kinetic controlled and is zero - order with respect to the solvent concentration. In the final region, the rate of shrinkage decreases tending towards equilibrium. As is apparent from Figure 4, an equilibrium was not observed in the final region of the kinetics curve. All the curves showed tendency to rise to a peak after a period of 15 minutes and then drop drastically. Another peak period was observed after 45 minutes. This fluctuation after a time of treatment of 15 minutes was contrary to the findings of earlier workers[42]. However other studies[42] on the shrinkage kinetics of polyethylene terephthalate fibre in tetrachloroethane showed a similar fluctuation, though on a minor scale, which was attributed to entanglements among the fibres while immersed in the swelling solvent. The small piece of object used by these earlier investigators to align the filaments in a parallel orientation weighed 6.57×10^{-4} gpd. This weight is much bigger than the one used by us as earlier indicated in section 2.2.2. Hence, it is probable that despite the weight attached to our polyethylene terephthalate filaments, much entanglement may still be expected. In another study, the time of treatment in methanol was kept constant and temperature was varied. A plot of change-in-length per cent against temperature is shown in Figure 3. It was found that a peak of maximum shrinkage occured at $42^{\circ}C$. A probable explanation may be that the crystallites formed at this temperature are just strong enough to support the swollen structure and further increase in temperature leads to their being melted as the process of secondary crystallization is being initiated.

3.3 EFFECT OF HEAT AND SOLVENT - TREATMENT ON THE DENSITY OF PET FIBRES

The density of a fibre is generally proportional to the amount of crystallinity within that fibre. Table 2 shows the densities of various PET fibre samples and the corresponding percentage crystallinities. It must be emphasised that the density changes due to the disorientation of ordered amorphous regions should be considered in the calculation of crystallinity values from density determinations[40]. Recent studies by Samuels[43] and Wilson[44]

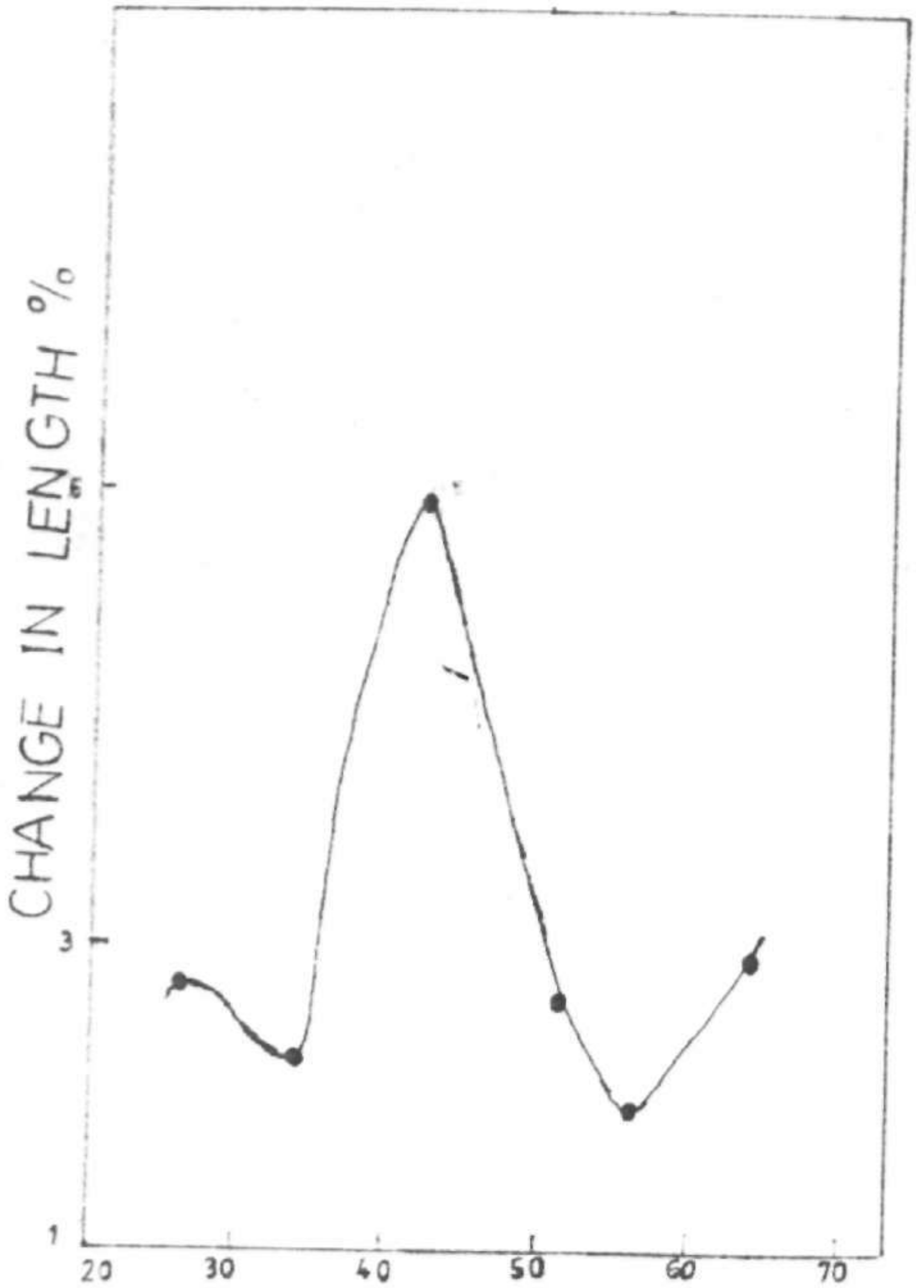


Figure 3 : PLOT showing change in length% of drawn PET FIBRES treated in methanol against temperature

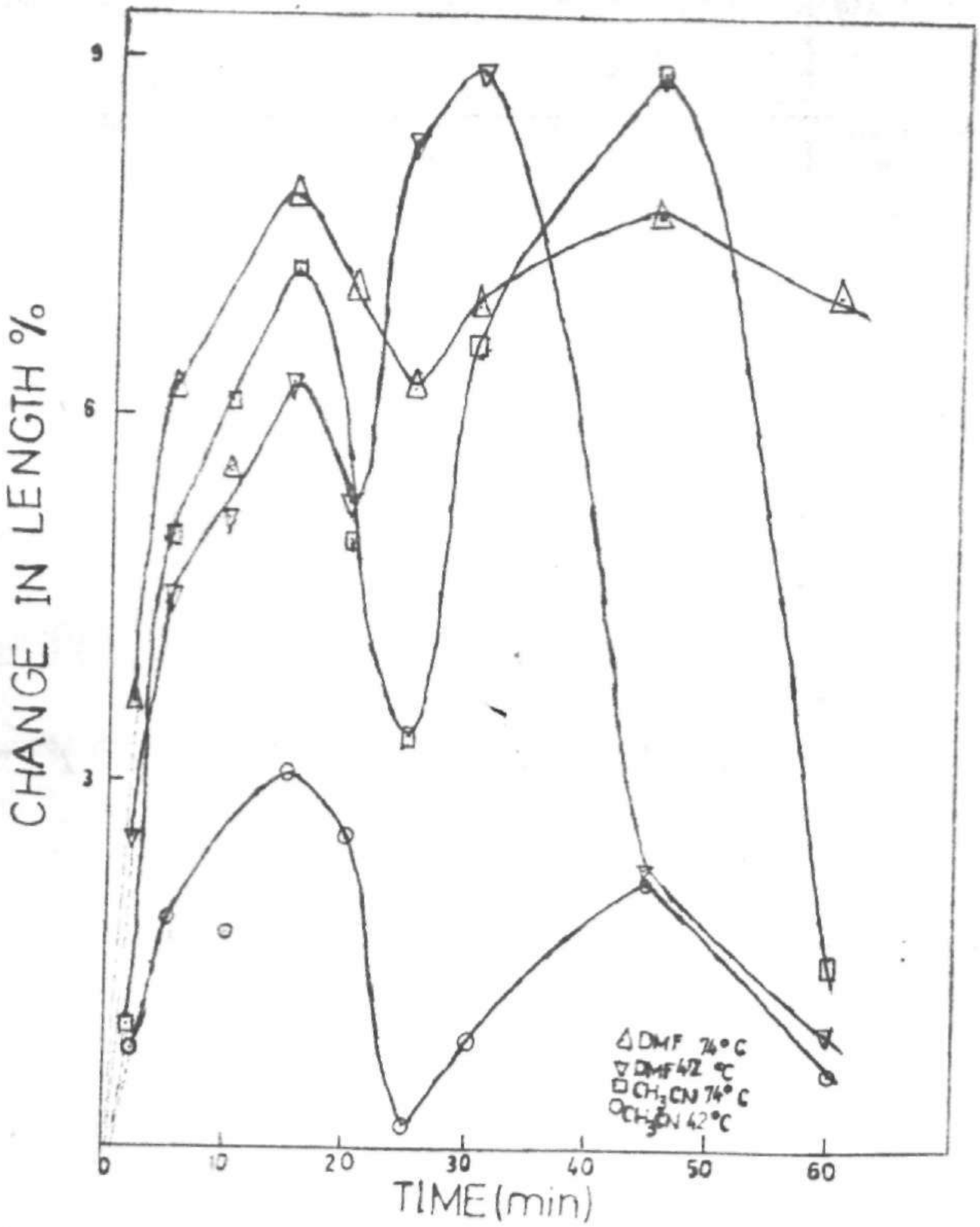


Figure 4 : PLOT showing change in length% of drawn PET FIBRES treated in DMF and acetonitrile against time

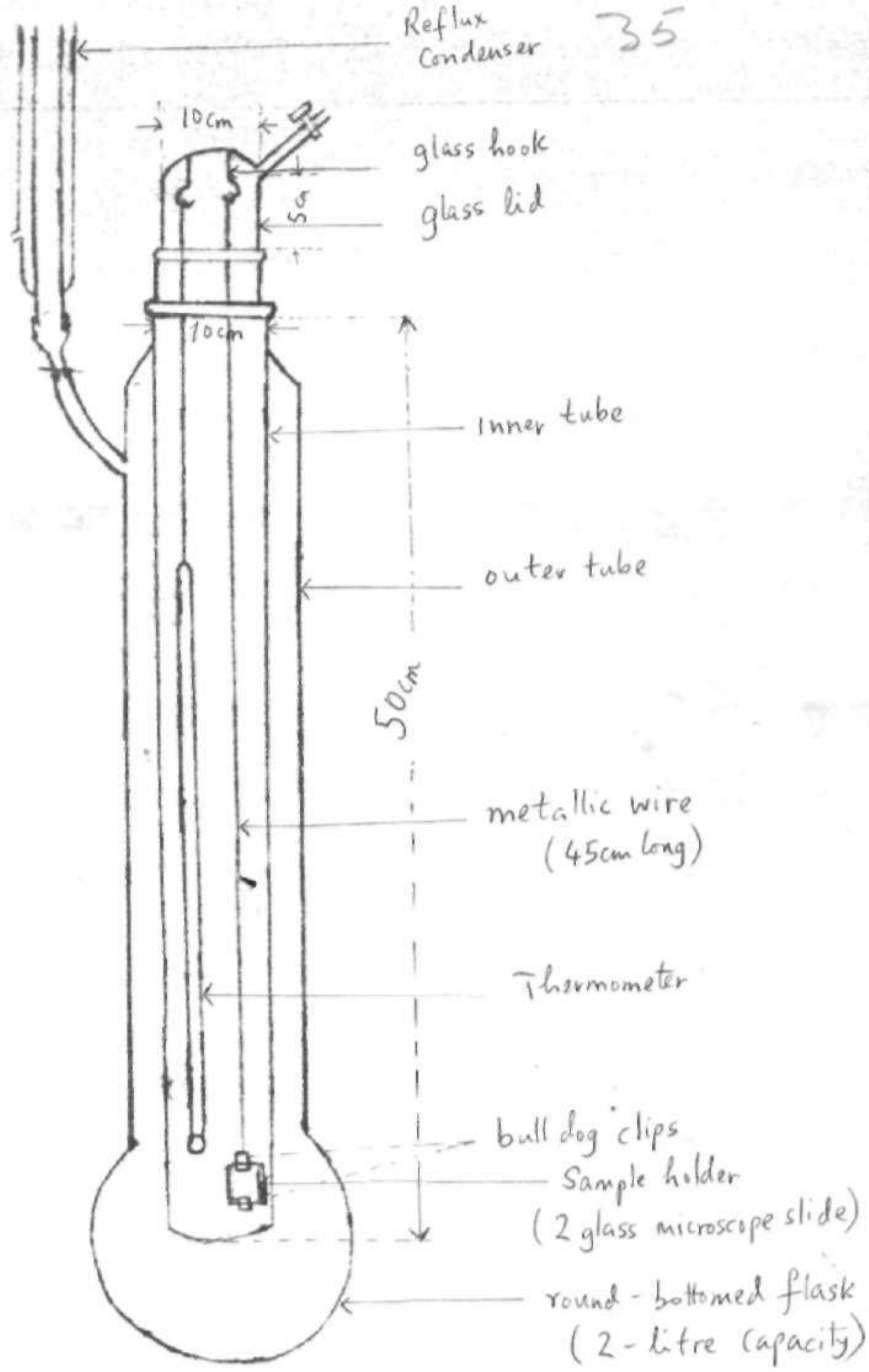


Figure 5: Apparatus used for heat-setting of fibre

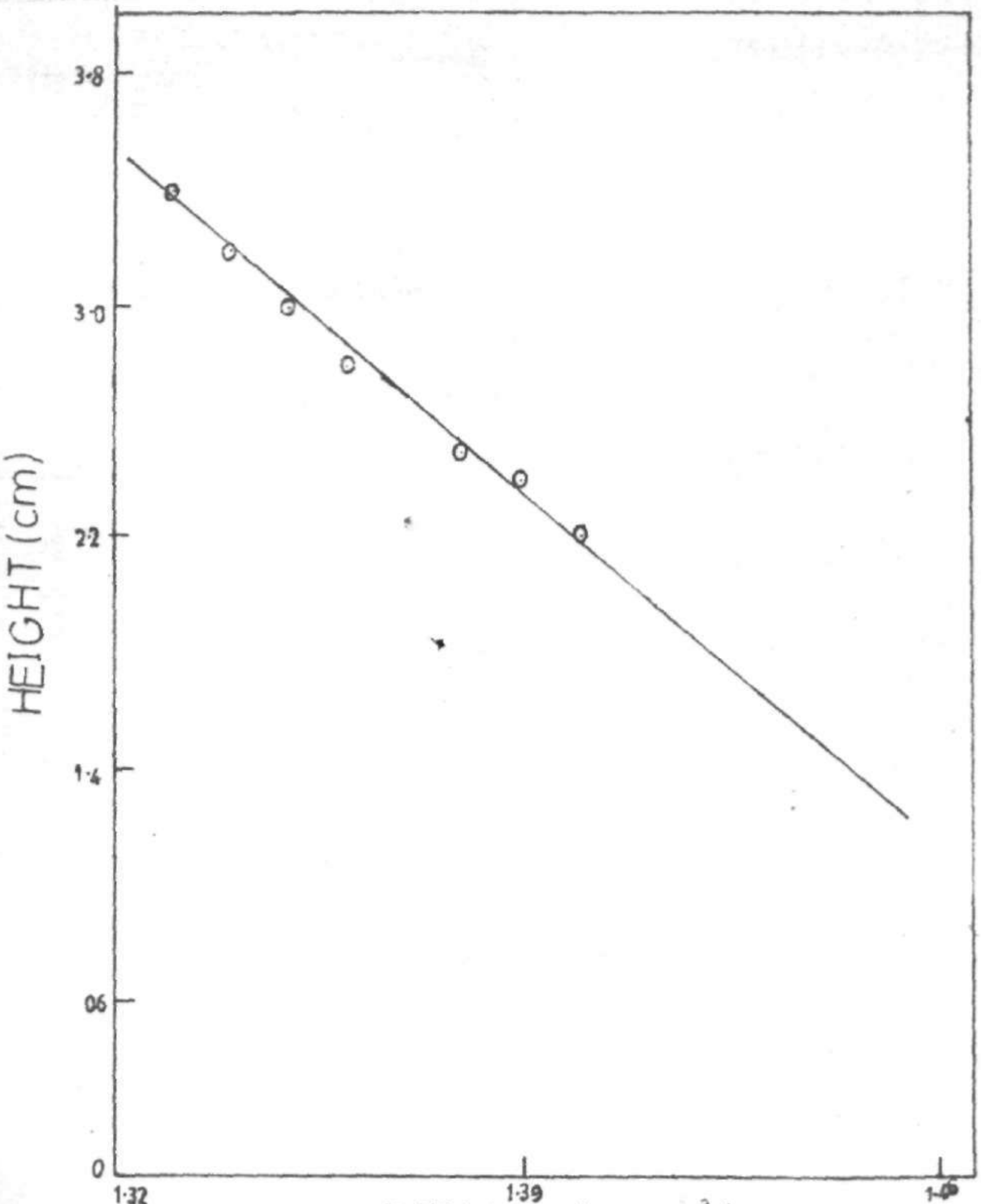


Figure 7: Calibration plot for density gradient column

TABLE 2

RESULTS OF DENSITY MEASUREMENTS

PET fibre Samples	Density (gcm^{-3})	Crystallinity %
Untreated	1.404	57.5
CH_3CN - treated	1.422	72.5
DMF - treated	1.452	97.5
HEAT-SET SAMPLES		
Heat-set at 99°C	1.410	62.5
" " 114°C	1.433	81.7
" " 130°C	1.450	95.8
DYED SAMPLES		
DMF treated-dyed 4 min	1.433	81.7
" " 64 min	1.381	38.3
" " 144 min	1.452	97.5

have shown that the semi-crystalline PET fibres can be treated as a two-phase system, and that macroscopic shrinkage results from a disorientation of oriented amorphous regions. Other studies have shown that crystallization by chain - folding is important near the polymer melting point[43]. In this study, heat-setting and solvent-treatment led to increase in density compared to the original, untreated sample. Density increased with increase in setting temperature (Figure 13). N,N-dimethyl formamide - treated sample had a higher density than the acetonitrile-treated sample. In certain cases densities of 1.452 gcm^{-3} suggesting crystallinities as high as 98% were recorded. Such values are considered unrealistic in that they suggest the virtual disappearance of an amorphous phase through selective chain scission at the interphase between crystalline and amorphous phases. This event was not observed in other studies[40]. It was then suggested that unrealistically high density values were as a result of preferential absorption of carbon tetrachloride (CCl_4) the heavier component of the carbon tetrachloride - n-heptane mixture in the density gradient column. A similar observation of unrealistically high density values of polyester after hydrolytic etching at a temperature of 180°C has been reported by Miyagi and Wunderlich[46]. These authors also attributed the high density values to preferrential absorption of the heavy component of the density gradient column (Carbon-tetrachloride - n-heptane). The surprising selective absorption of carbon tetrachloride, a non - interacting solvent, must be attributed to the structural changes produced by DMF treatments in the unrestrained condition at higher temperatures and is a reflection of the extent of void formation and the porosity of the resulting structure[40]. The occurence of unrealistically high density values can be avoided if a liquid system, such as calcium nitrate solution which does not permit preferential absorption, is used. This is illustrated in Table 3 which shows density values observed with DMF - treated samples at 140°C and 150°C for 15 minutes.

In the same studies,[40] Critical Dissolution Time Concept was introduced. Critical Dissolution Time (CDT) measurements suggest that increases in density as a result of DMF treatments below 120°C must be associated with the formation of small crystallites but at temperatures above 120°C, a large increase in crystallite size and stability is suggested by the sudden increase in CDT. The increase in density or crystallinity observed with increasing heat-setting temperature may thus be accounted for in two ways: increase in heat-setting temperature introduces more chain-folding sites which serve as nucleating centres and the overall higher stability of the new structure confers greater stability on the crystallites which grow to larger sizes.

3.4 EFFECT OF SOLVENT TREATMENT ON DYEABILITY

The chemical potentials of the dye molecule in the solution and in the fibre phases may be represented thus:-

TABLE 3

Density and crystallinity of polyester yarns after treatment in DMF (unrestrained) at various times and temperatures determined by two liquid systems in density gradient columns.

Treatment Conditions		Liquid System			
		Heptane - ccl4		Water - calcium nitrate	
		Density(g/cm^3)	Cryst.%	Density(g/cm^3)	Cryst. %
60°C,	180 min	1.383	40	1.386	42.3
80°C,	180 min	1.387	43.3	1.388	44.4
100°C,	180 min	1.391	46.7	1.392	47.5
120°C,	180 min	1.396	50.8	1.395	49.8
140°C,	15 min	1.428	77.5	1.401	54.8
140°C,	180 min	1.444	90.8	1.409	61.7
150°C,	2 min	1.440	87.5	1.400	53.9
150°C,	15 min	1.447	93.3	1.400	54.3
150°C,	180 min	1.450	95.8	1.401	55.4

(AFTER WEIGMANN et al [40])

$$\mu_s = \mu_s^{\circ} + RT \ln a_s - - - - - (1)$$
$$\mu_f = \mu_f^{\circ} + RT \ln a_f - - - - - (2)$$

when a dynamic equilibrium has been established (1) and (2) become equal and hence the following relationship holds:-

$$\mu_s^{\circ} - \mu_f^{\circ} = -\Delta\mu^{\circ} = RT \ln \frac{a_f}{a_s} - - - - - (3)$$

where us and uf are the chemical potentials of the adsorbate in the external and adsorbant surfaces respectively, a_s and a_f are the corresponding activities

μs° and μf° are the corresponding standard chemical potentials. The quantity, $-\Delta\mu^{\circ}$, which represents the change in standard chemical potential or standard molal free energy in the transfer from the external to the adsorbant phase is known as the affinity. It is evident from (3) that for partition to occur between the external and adsorbant phases, a_f must be greater than a_s. For very dilute concentrations, as in a disperse dye system, the quantity $\frac{a_f}{a_s} \simeq \frac{C_b}{C^n{}_f} = K$

where C_b = Concentration of bound dye

C_f = Concentration of free dye

K = Partition coefficient.

and n may assume a non - zero positive value which accounts for non-linearity in the adsorption istherm.

This relationship holds even within the voids in the fibre structure, since the currently accepted view is that diffusion of dyes into the fibre occurs through the agency of water-filled microvoids. According to the pore model of diffusion which is believed to operate(40) in solvent - induced modified fibre, a substantial proportion of the dye molecules that penetrate the fibre become adsorbed and immoblized, thus reducing the effective uptake rate with time. Mathematical analysis of the problem shows that for a large liquour to goods ratio, the following relationship holds to a first approximation:

$$\frac{Mt}{M_\infty} \propto \left(\frac{DT}{a^2}\right)^{1/2}$$

while for a small liquour to goods ratio, the corresponding relationship is:-

$$\frac{Mt}{M_\infty} \propto \left(\frac{Dt}{a^2}\right)$$

where Mt and M_∞ are quantities of dye taken up at time t and after an infinite period of time ($t \longrightarrow \infty$), a, the raduis of the fibre and D the diffusion coefficient of dye in the fibre.

Berndt et al[47] has enumerated other factors such as dyestuff concentration, temperature, stirring, and pH which affect the reproducibility of disperse dyeing of polyester fibres. It was shown in section 1.3 that increase in temperature accelerates dye diffusion within the fibre while increases in dye concentration and stirring rate increase dye-uptake. Results from Imperial Chemical Industries (ICI) show that between pH 2.8 and 7.0 diffusion can occur without fibre damage for 2 hours at 160°C[48]. Berndt[47] suggested that these difficulties can be overcome by determining a relative dye-uptake in which the dye-uptake of the test sample is normalized by the dye-uptake of an untreated, control sample dyed simultaneously in the same bath. This technique was used in this investigation and relative dye-uptakes are therefore used to characterize the dyeability of the solvent-treated samples. As these values do not represent equilibrium values, they are more reflective of dye diffusion characteristics.

Tables 4 and 5 give values for the dye absrobed per cent by fibres which had been pretreated with N, N-dimethyl-formamide and acetonitrile. These values are presented as graphs of dye absorbed per cent against square root of time of dyeing in figure 8. A characteristic feature of these graphs is the occurence of a temporary saturation phase between 36 and 100 minutes in the dyed fibres. A sudden sharp rise is then noticed between 100 and 144 minutes. This effect is more apparent for the DMF - treated fibres. The effect of the solvent-treatment is to create voids within the fibre structure and thereby causing the dyestuff to migrate more rapidly and to achieve saturation at much earlier dyeing time. In other studies[49] a close correlation was observed between dye-uptake and void volume, calculated from density data. This observation contrasts with that of I.C.I. workers who recommended a minimum period of 2 hours to achieve levelness of shade at $130^{o}C$.[48]. They also showed that better depth of colour can be obtained at $120^{o}C$ without a carrier than at $100^{o}C$ with a carrier and that with some exceptions it was undesirable to use a carrier at $120^{o}C$. Under the treatment conditions used in this work i.e. $74^{o}C$ and 15 minutes, acetonitrile was found to be a rather weak plasticizer. Compared to the untreated sample, it improved dye-uptake by 3%. DMF treatment enhanced relative dye uptake by 61%. Compared to acetonitrile - treated samples, DMF - treatment also resulted in improved diffusivity, as is evident from the slope of the initial portion of the rate of dyeing curves shown in Fig. 8

3.5 EFFECT OF SOLVENT - TREATMENT AND DYEING ON MECHANICAL PROPERTIES OF PET FIBRES.

Table 6 illustrates the mechanical properties of the untreated, untreated and dyed, solvent-treated and solvent-treated and dyed samples. Figures 10a, 10b and 10c also show the stress-strain curves for solvent-treated and some dyed PET fibres. A full characterisation of the effect of solvent-induced modification of fibre structure on its dyeability cannot be achieved unless cognisance is also taken of the side effects of such treatment on mechanical properties. Ugbolue and Aula[50] observed that disperse dyes initially caused a reduction in tensile strength of undrawn PET fibres and that at saturation the original tensile strength was restored. They also observed[50] a monotonic decrease in the extensibility as well as a monotonic increase in the initial modulus with dyeing time. Results from drawn fibres in this study indicate a decrease in the tensile strength after a dyeing period of 144 minutes, an increase in extensibility and an increase in initial modulus. The decrease in tensile strength and the increase in extensibility suggest that the dye is acting as a plasticizer. Okajama et. al[51] have in their studies on the dichroism of the PET - disperse dye system confirmed that disperse dyes act as weak plasticizer. They have also shown[51] that a distribution of lateral order exists in the amorphous region and that dye molecules do not distribute homogeneously throughout the entife amorphous region but exist only within the region of lowest lateral order. In considering the variation in the intial modulus, several forces come into play. The value of the rubbery modulus depends firstly on the volume concentration of the crystalline lamellae which act simultaneously as rigid fillers and as physical cross - links[52]. Secondly this modulus is a function of the number, the average length and the conformation of the amorphous segments between the lamellae[52].

Table 6 also shows that DMF and acetonitrile treatment led to a weakening of the tensile strength of PET fibres, with the DMF having a more pronounced effect. An increase in extensibility was observed for the DMF - treated fibres while no apparent change in extensibility was found for acetonitrile treated fibres.

TABLE 4

PERCENTAGE DYE ABSORBED BY DMF - TREATED PET FIBRES

Time of Dyeing (min)	Absorbance	Concentration ($g/cm^3 \times 10^3$)	Dye absorbed %
4	0.100	2.75	1.38
16	0.130	3.50	1.75
36	0.170	4.75	2.38
64	0.172	4.76	2.38
100	0.175	4.78	2.39
DMF-144(treated)	0.235	6.63	3.31
144(untreated)	0.150	4.13	2.06

TABLE 5

PERCENTAGE DYE ABSORBED BY ACETONITRILE - TREATED PET FIBRES

Time of Dyeing (min)	Absorbance	Concentration $(9/cm^3 \times 10^3)$	Dye absorbed %
4	0.055	1.50	0.75
16	0.070	2.00	1.00
36	0.080	2.25	1.13
64	0.095	2.50	1.25
100	0.095	2.63	1.31
144 (CH_3 CN-treated)	0.155	4.25	2.13
144 (untreated)	0.149	4.13	2.06

TABLE 6

THE MECHANICAL PROPERTIES OF VARIOUS TREATED PET FIBRES

Measurements	Un-treated	Un-treated dyed for 144 min	DMF-treated	DMF-treated 4 min dyed	DMF-treated 64 min dyed	DMF-treated 144 min dyed	CH_3CN treated	CH_3CN treated 4 min dyed	CH_3CN treated 64 min dyed	CH_3CN treated 144 min dyed
Mean Tensile strength (gf/tex)	3.23	2.65	2.57	2.42	2.19	2.67	2.68	2.50	2.14	2.83
Mean extension-at-break %	12	13	13.5	10	9	12	12	12	8	10
Initial Modulus (gf/tex)	25	32.69	30.31	33.02	17.31	20.69	18.67	24.68	23.33	29.50
Secant Modulus (gf/tex)	26.92	20.38	21.42	24.20	24.33	22.25	22.33	20.83	26.75	28.30

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A decrease in initial modulus is to be expected from theory and while this was observed for acetonitrile-treated fibres, an increase was found for DMF - treated fibres. Apart from the anomaly represented by the high value found for the initial modulus of DMF - treated fibres, the changes in mechanical properties are consistent with a fibre which is undergoing a reduction in orientation. The extent to which this reduction manifests itself in terms of observed changes depends on the physical characteristics of the fibre, especially its degree of orientation and crystallinity, treatment conditions as well as the effectiveness of the plasticizing solvent. The treatment conditions used, i.e. 74^{o}C and 15 minutes, is considered not sufficiently drastic to produce very marked changes when acetonitrile is used as the plasticizing solvent because of the lower interacting ability of acetonitrile. The constancy of the extensibility value, despite acetonitrile treatment may be understood in the light of the preceeding statement. It is probable that extensibility may well be a less sensitive test for evaluating mechanical properties of modified polyethylene terephthalate. A similar observation is recorded for the extensibility of PET samples heat set at lower temperatures (Table 2). The unusually high value of the initial modulus for DMF - treated fibre is comparable to a similar observation in the solvent - treatment of nylon 66 yarns.[53] This effect was thought to be associated with a possible re-orientation of hydrogen bonds or with the withdrawal of bound

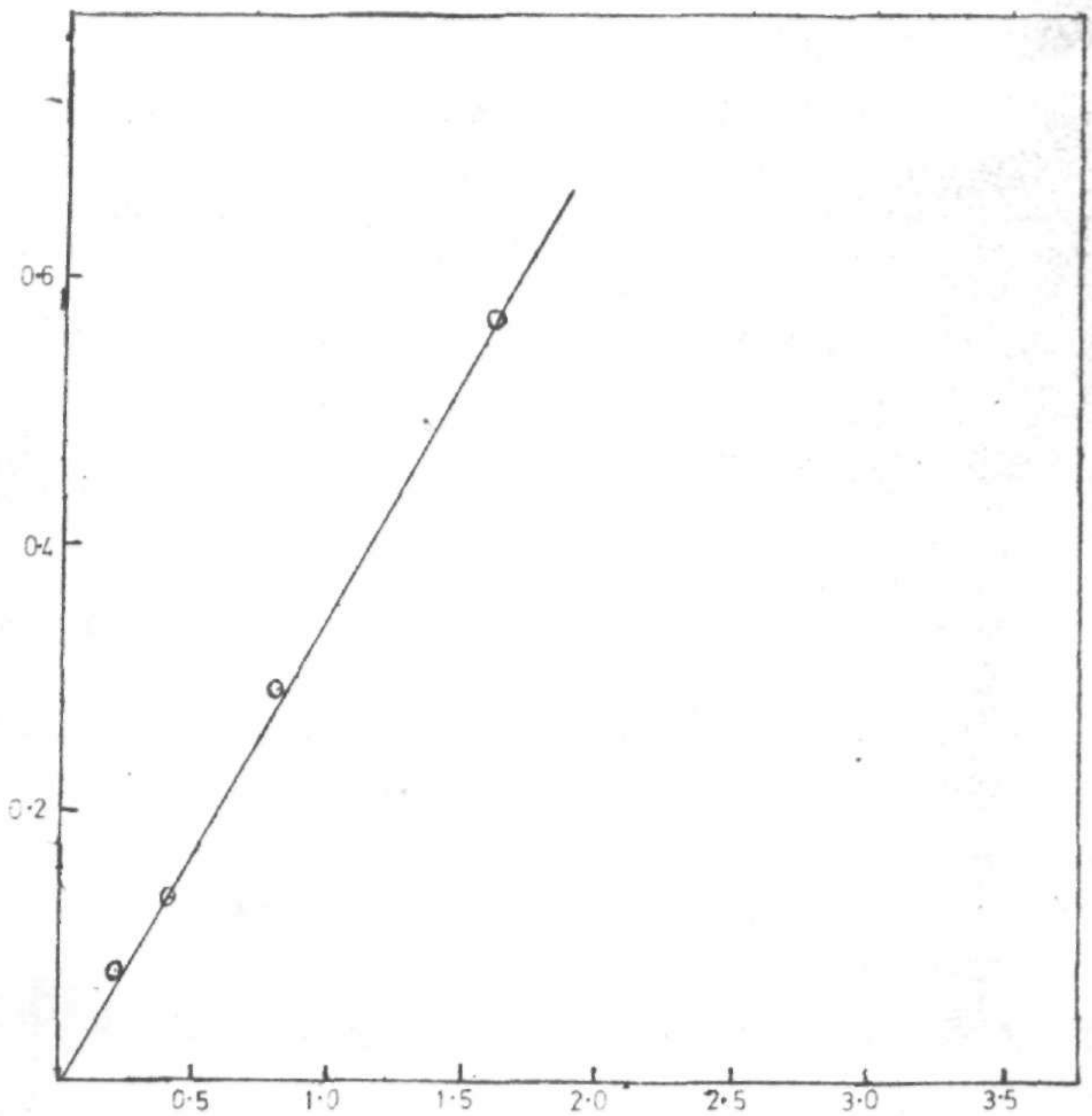

Figure 7: Calibration plot of Dispersol Red B-2B

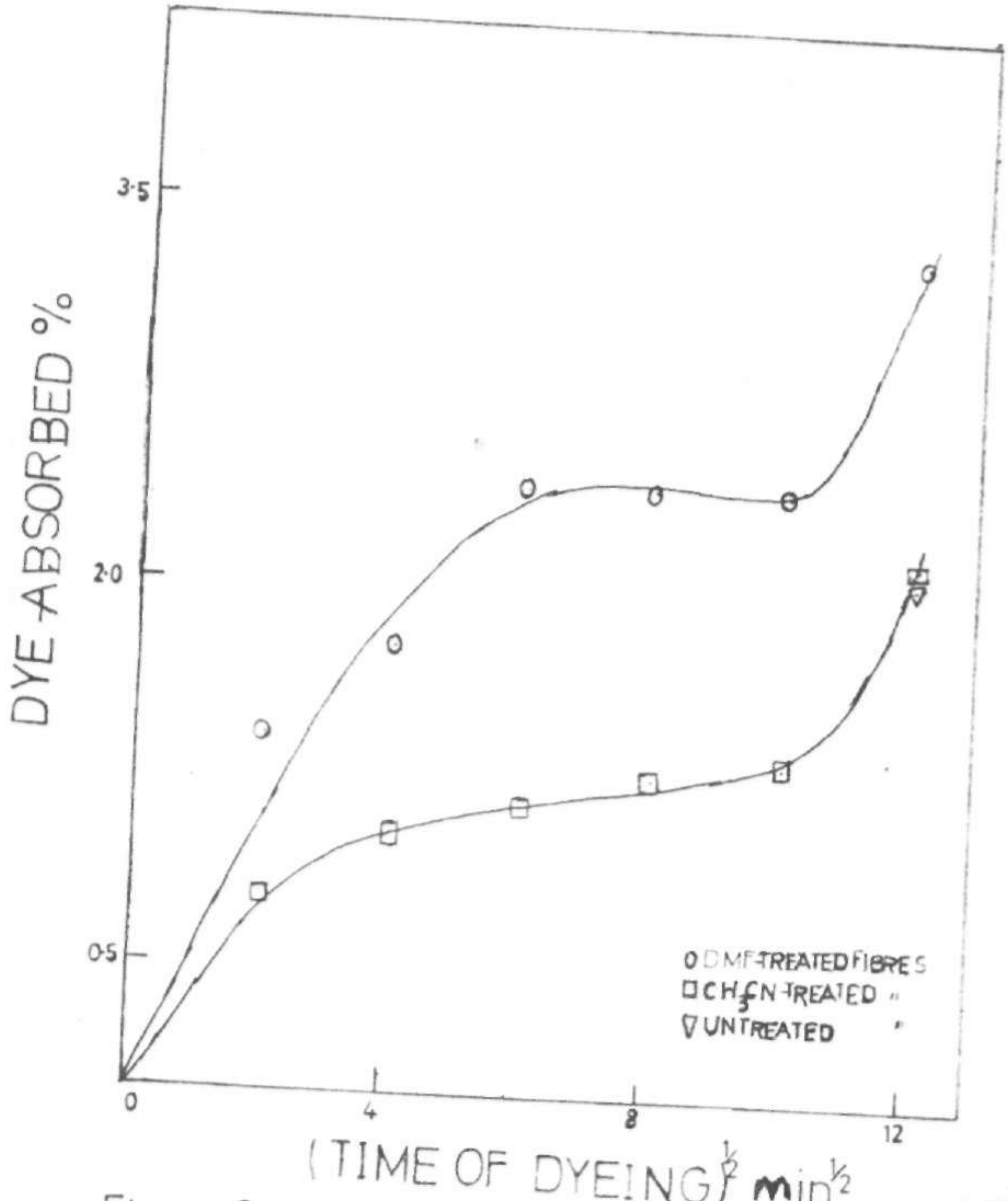

Figure 8 : Rate of dyeing curves

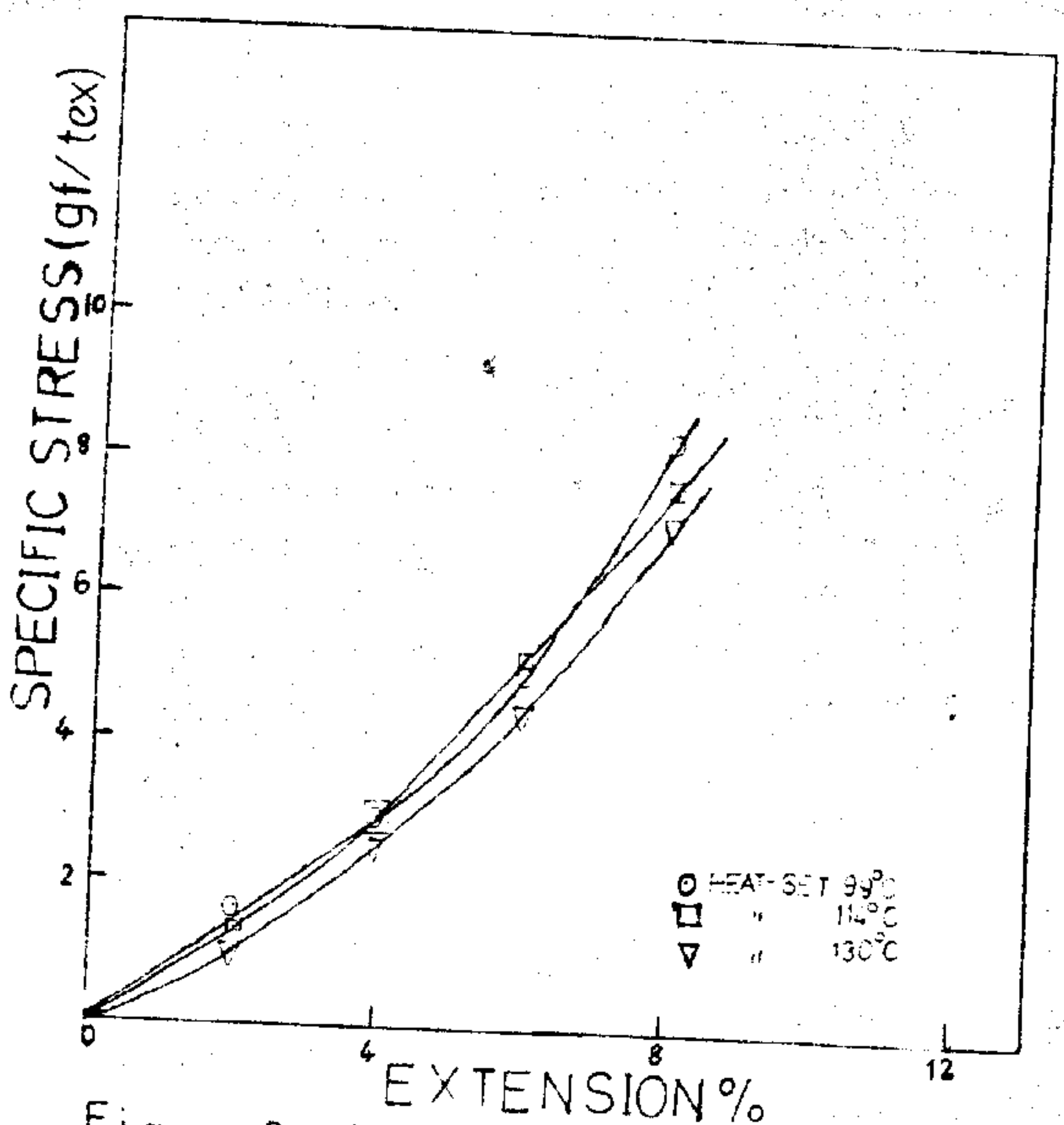

Figure 9: stress - strain curves for heat-set PET fibres

12

EXTENSION %

Figure 10a stress-strain curves for untreated and solvent-treated PET fibres

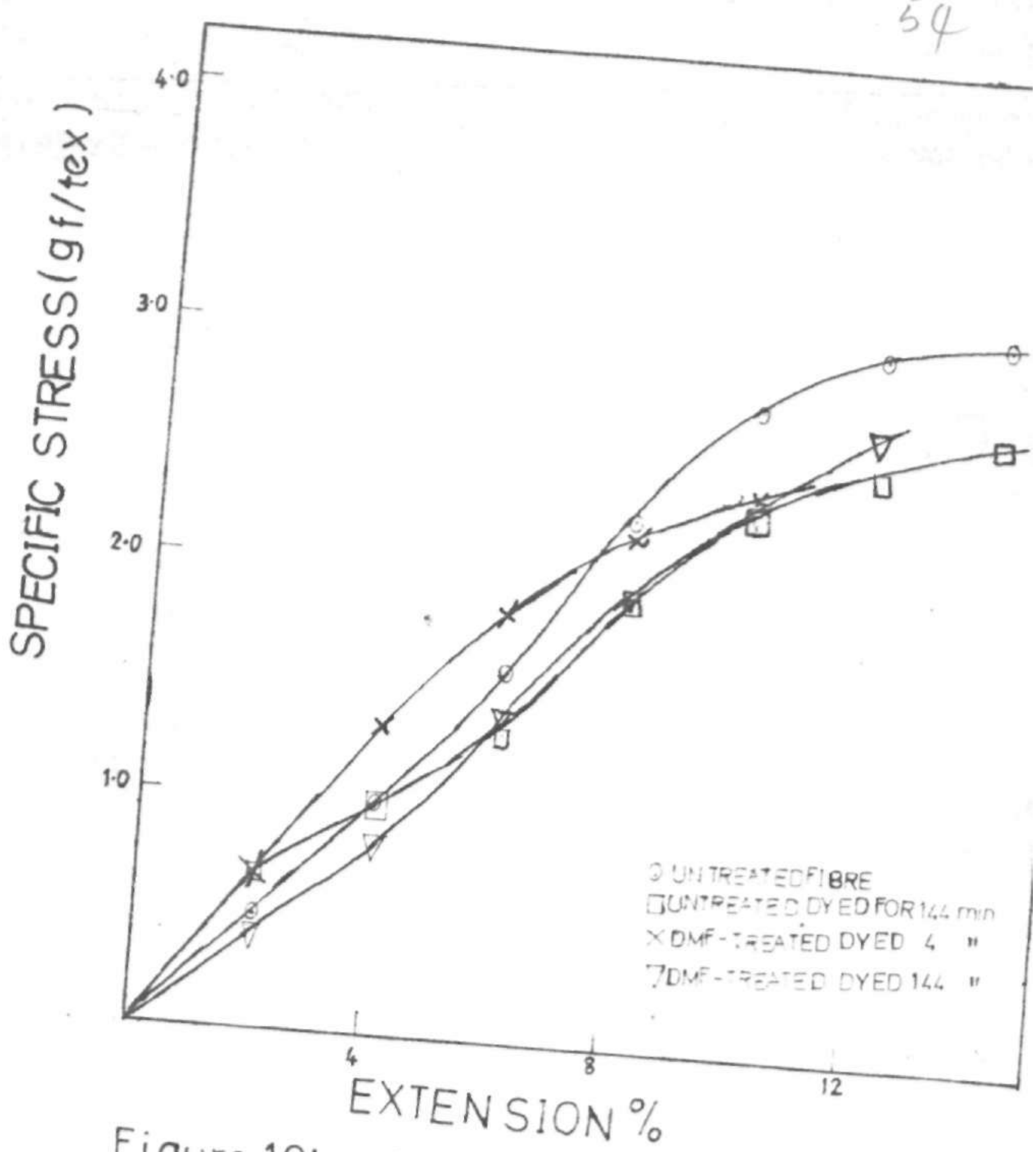

Figure 10b : stress-strain curves for some untreated and DMF-treated dyed PET fibres

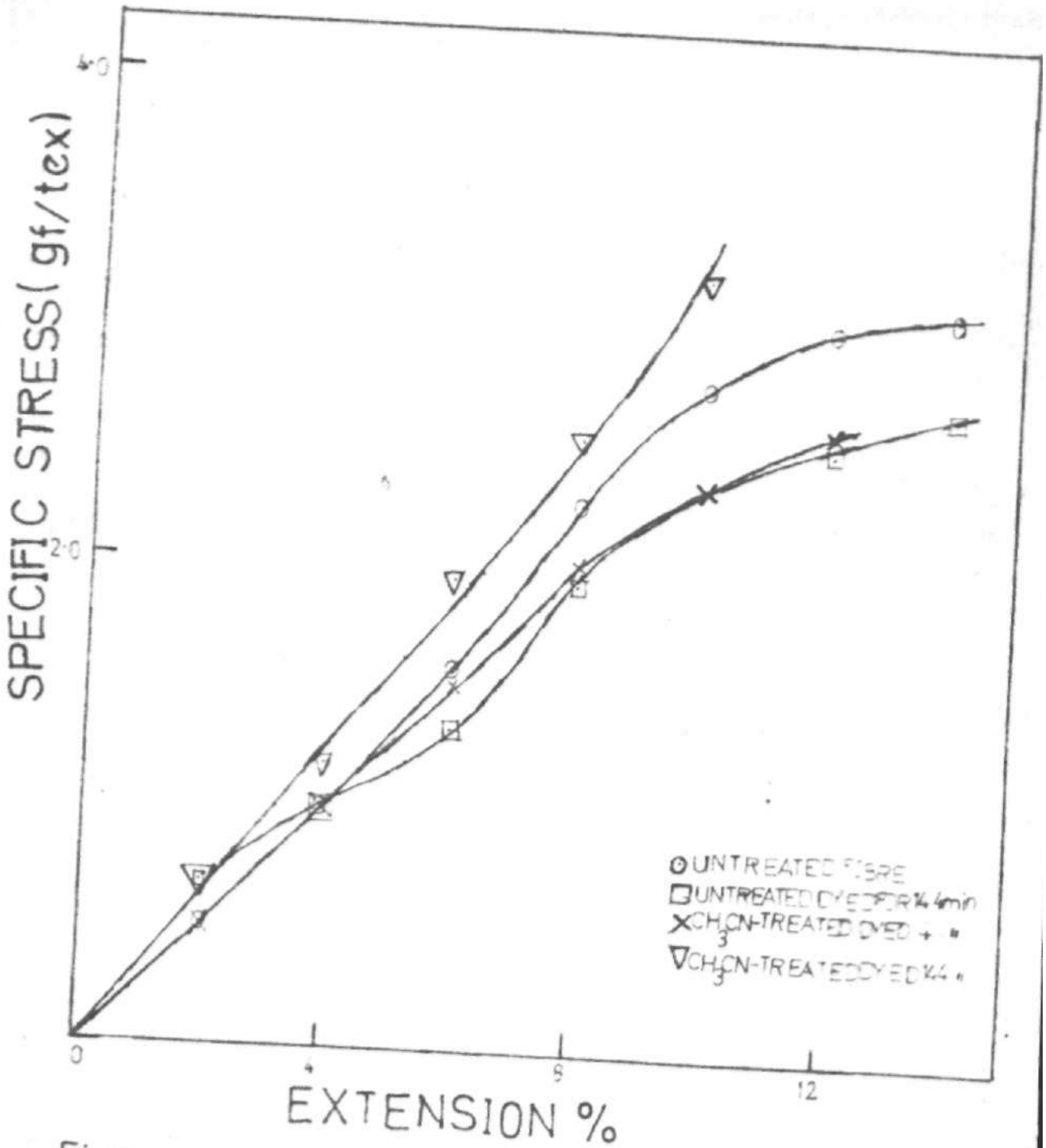

Figure 10c : stress-strain curves for some untreated and CH_3CN-treated dyed PET fibres

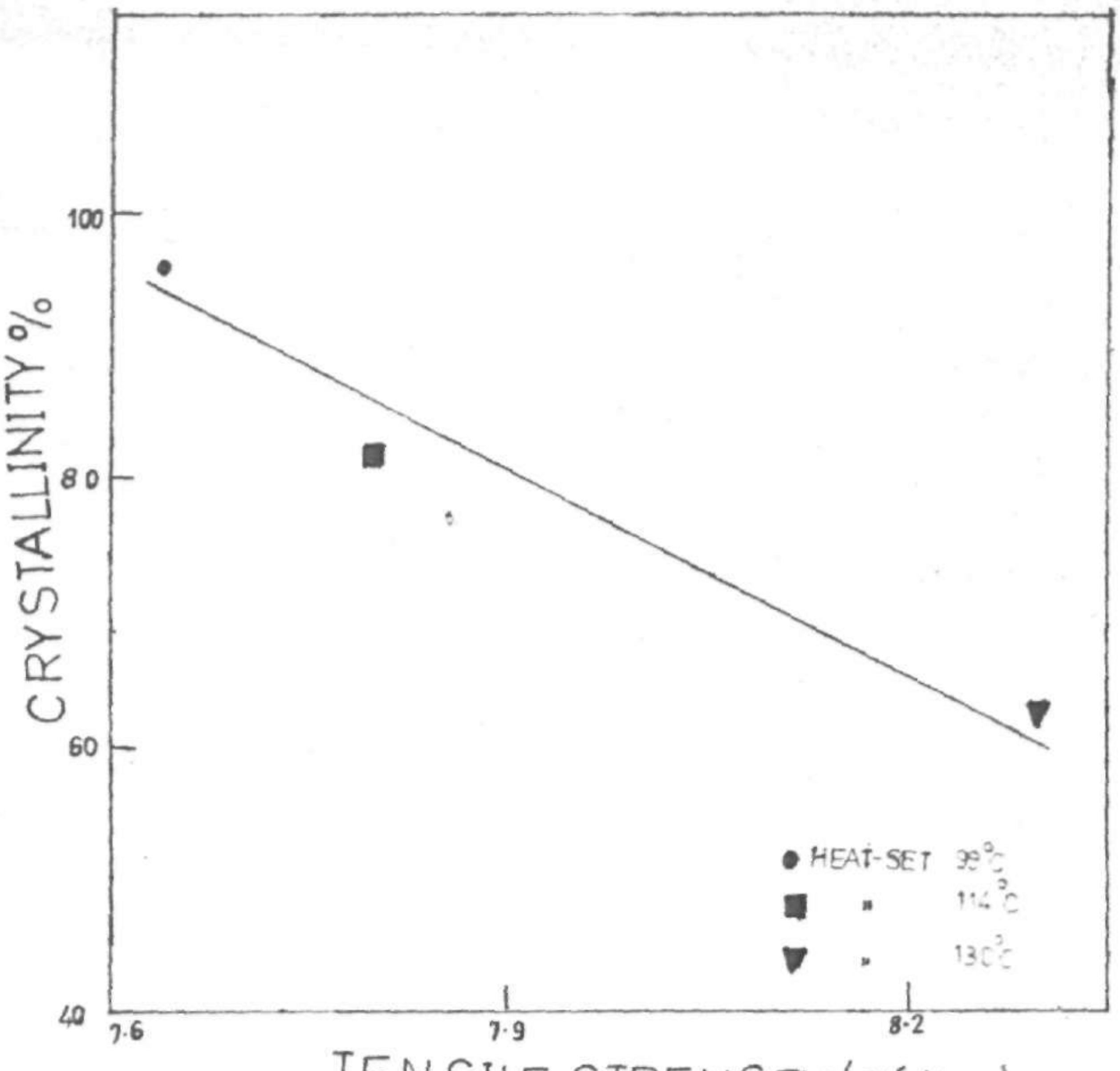

Figure 11: PLOT showing variation of crystallinity with tensile strength of drawn PET fibres heat-set at various temps.

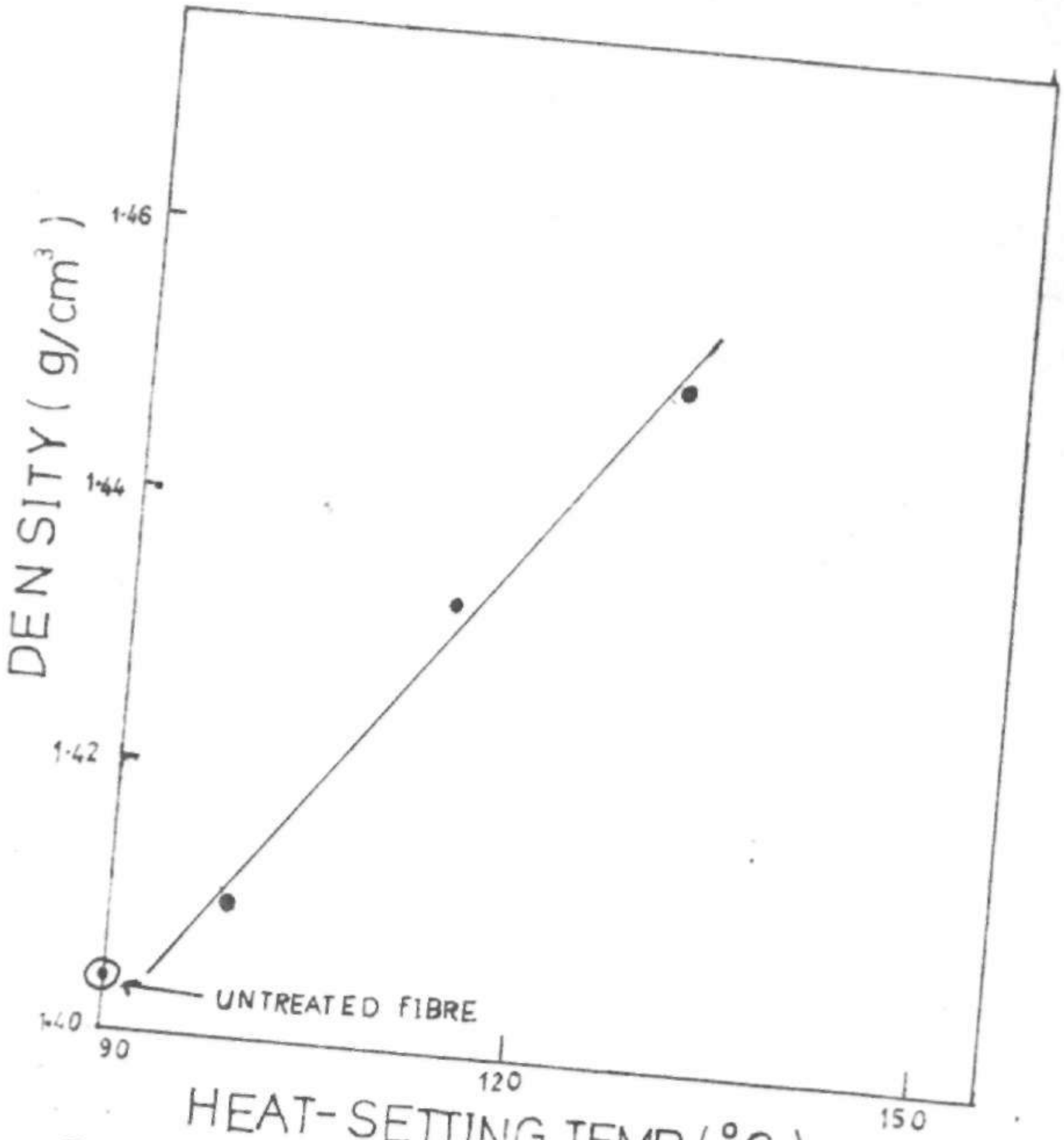

Fig.13 PLOT showing variation of density with heat-setting temp. of PET fibres

water. On this basis, a plausible explanation may be attempted for the high initial modulus of DMF - treated fibres. N, N - dimethyl formamide is a strong hydrogen-bonding solvent which is difficult to extract completely from the fibre matrix. Some residual DMF is left after solvent-treatment although this has no effect on the dyeability of the fibres[40]. The presence of hydrogen bonds could give rise to the high initial modulus.

The mechanical properties of the solvent-treated and dyed fibres exhibit a noticeable periodicity. The values of the main parameters namely, tensile strength, extension - at - break per cent and initial modulus were lowest after dyeing for 64 minutes. This time falls within the dye saturation period illustrated in Figure 8. Hence the lowering of the mechanical properties at this time is thought to be due to plasticization by the dyes since it has been shown[50] that disperse dyes act as weak plasticizer which disrupts the lateral order of the oriented amorphous regions. The gradual build-up in mechanical properties of drawn, solvent-treated PET fibres after 144 minutes of dyeing may probably be due to the effect of saturation with the dyes acting as rigid fillers. However, further investigation in this area would be required to establish this conclusively.

3.6 CONCLUSIONS

The following conclusions have been drawn from this investigation:-

(1) N,N-dimethyl-formamide is a more effective plasticising solvent than acetonitrile for PET fibres.

(2) Treatment of polyethylene terephthalate filaments in DMF at 74°C for 15 minutes prior to dyeing enhanced relative dye-uptake by 60%.

(3) When compared with pressure dyeing of polyethylene terephthalate at 130°C, which has been found to be more effective than carrier dyeing at 100°C, PET treated with a highly interacting solvent like DMF achieves saturation after 36 minutes of dyeing compared to 2 hours required for pressure dyeing.

(4) For purposes of improving the dyeability of PET fibre, DMF is 20 times more effective than acetonitrile after treatment in both solvents at 74°C for 15 minutes prior to dyeing for a period of 144 minutes.

(5) The deterioration of useful mechanical properties of the PET fibre subjected to solvent-treatment at 74°C prior to dyeing is not drastic.

(6) Considerable savings in dyeing costs may be realised by employing DMF - solvent treatment of PET and dyeing at 100°C than by using pressure or high temperature dyeing and carriers.

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