

## **Shrinkage of Polyester Fibre in Selected Chlorinated Solvents and Effects on Dimensional Stability of the Fabric.**

A.V. Popoola, A.O. Adetuyi and G.O. Oyeleke

*Department of Chemistry, Federal University of Technology, P.M.B. 704, Akure, Ondo State, Nigeria.*

---

**Abstract:** Polyester fibres were isothermally treated with four chlorinated solvents; perchloroethylene (PCE), trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE) and tetrachloromethane (TCM). Measurement of the longitudinal shrinkage of the treated fibres was carried out at room temperature for 30, 60, 150, 300, 450, 600, 750, 900 and 1800 seconds that was found to be sufficient to establish dynamic equilibrium conditions for each of the solvents. From the results, a trend of 1,1-DCE > PCE > TCE > TCM was observed for the shrinkage values which showed that the solvents exhibited behaviour that cannot be explained in terms of the variations in their boiling points and molecular weights values. Solubility parameter values ( $\delta$ ) of the solvents were however, found to be the overriding factor as it followed the above trend. The treatment has been able to provide a means of improving polyester fibre structure to suit its use in commercial applications and also revealed that the best among the four solvents in term of effecting minimal change on the structure and quality of the fabric during laundry will be TCM.

**Keywords:** Polyester, chlorinated, solvent, shrinkage, solubility parameter, overriding, fabric.

---

### **I. Introduction**

Polyesters are polymers made by condensation reactions taking place between small molecules, in which the linkage of the molecules occurs through the formation of ester groups. Polyesters can also be made by interaction of a dibasic acid with an alcohol [1]. A polyester fibre has a great diverse end use and the principal one among them is in the textile manufacturing industry.

One of the most obvious manifestations of the interaction between organic solvents and polyester (polyethylene terephthalate) (PET) filaments is the longitudinal shrinkage that the filaments undergo on exposure to solvents [2]. The modification of the fibre structure has been associated with simultaneous recrystallization process that will enhance rapid diffusion of high energy disperse dye, which could be applied at atmospheric conditions without the use of a carrier or high temperature/pressure equipment. In contrast to the thermal shrinkage, during which the input of thermal energy results in a localized “melting” of the internal structure, permitting the development of chain mobility, the chemical energy during solvent treatment is presumably generated by molecular interactions between polyester and solvents, leading in extreme cases to the formation of solvated bonding sites with the polymer structure [3].

The compaction that accompanies shrinkage is useful in obtaining greater weight, density, bulkiness, higher strength and improved cleavage properties [4]. Ugbole and Popoola [2] reported that solvent treatment leads to a high degree of swelling and formation of crystallites at elevated temperatures and that upon removal of interacting solvents and subsequent stabilization of the swollen structure, cavitation and void formation are observable

Glass transition temperature ( $T_g$ ) of textile fibre marks the temperature at which substantial segmental mobility in the polymer chains becomes possible [5]. This has been noted to decrease during solvent treatments by Popoola [6] due to the plasticizing action of the solvents [7].

A consequence of the internal structural re-arrangement of the polyester chains during solvent treatment is observed in the mechanical and dimensional properties of the treated PET fibres. The magnitude of the changes is dependent upon the orientation and crystallinity of the fibre and upon external variables such as temperature, tension, time and environment.

The intent of this study is to treat PET fibre in four commercial chlorinated solvents in order to determine their effects on the dimensional stability as well as the fibre response to different environment to which they may be exposed, both in the processing and in use stages.

### **II. Methodology**

Twenty (20) pieces of the purified polyethylene terephthalate (PET) fibres of 20cm long were measured and treated in four selected chlorinated solvents; perchloroethylene (PCE), trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE) and tetrachloromethane (TCM). A transparent glass tube was filled to mark with each of the above named chlorinated solvents. A strand of the already measured PET filament which has been attached to a light weight (0.5g) to remove stress and also to straighten it was suspended separately in a

100 ml measuring cylinder filled with the chlorinated solvents for 30, 60, 150, 300, 450 and 600, 750, 900 and 1800 seconds respectively at room temperature. The treated PET filaments were air-dried at room temperature and the difference in length before and after the solvent treatments was measured while the amount of shrinkage was calculated in percentage of the initial length.

### III. Results and Discussion

#### 3.1 Results

**Table 1: Results of Time of Treatment and Shrinkage of PET Fibre in the Chlorinated Solvents.**

Pretreatment Time (sec)	Shrinkage (cm)			
	TCM	PCE	TCE	1,1 DCE
30	0.14±0.03	0.24±0.03	0.16±0.05	0.24±0.04
60	0.16±0.01	0.24±0.04	0.18±0.05	0.28±0.05
150	0.18±0.05	0.26±0.05	0.20±0.03	0.30±0.03
300	0.20±0.03	0.28±0.04	0.22±0.02	0.32±0.03
450	0.22±0.03	0.30±0.03	0.24±0.04	0.34±0.02
600	0.24±0.03	0.32±0.03	0.26±0.05	0.36±0.04
750	0.26±0.05	0.34±0.02	0.28±0.04	0.38±0.05
900	0.28±0.03	0.36±0.04	0.30±0.03	0.40±0.02
1800	0.28±0.03	0.36±0.04	0.30±0.05	0.40±0.02

Results are average of Twenty (20) Determinations ± Standard Deviation.

**Table 2: Time of Treatment and Percentage Shrinkage of PET Fibre**

Pretreatment Time (sec)	Shrinkage (%)			
	TCM	PCE	TCE	1,1 DCE
30	0.70	1.00	0.80	1.20
60	0.80	1.20	0.90	1.40
150	0.90	1.30	1.01	1.50
300	1.00	1.40	1.10	1.60
450	1.10	1.51	1.20	1.70
600	1.20	1.60	1.30	1.80
750	1.29	1.70	1.40	1.89
900	1.40	1.80	1.50	2.00
1800	1.40	1.80	1.50	2.00

(Calculated from table 1)

#### 3.2 Discussion

The results of the shrinkage observed by treating the polyester in the selected chlorinated solvents are presented on Table 1 and the percentage shrinkage values contained in table 2.

In all the determinations, 20 samples were used in each case and the results shown in the tables were calculated on the mean values from the entire population chosen. For ease of comparison, Table 2 reveals the results for the shrinkage values at a glance. It was observed from Tables 1 and 2 that the least shrinkage was caused by TCM having a value of 14% for 30s of contact and 28% for 1800s. This was closely followed by TCE with 16% shrinkage for 30s and 30% for 1800s, PCE and 1,1-DCE gave higher values of shrinkage in that order showing 20% for 30s and 36% for 1800s for PCE and 24% for 30s and 40% for 1800s in case of 1,1-DCE.

Certain factors may be responsible for this trend which may include

- (1) the molecular mass and size of the solvents vis-à-vis the ability of the solvents to penetrate the polyester matrix to effect shrinkage.
- (2) the solubility parameters of the liquids which define the ability of the polymer: liquid pair to interact on the basis of similar forces of operation.

Since the polymer fibre being used in this case is same, it is safely assumed that factors such as its crystalline/amorphous ratio, transition temperature and other morphological factors that can influence liquid

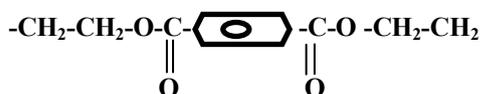
sorption and shrinkage are the same for all the cases of treatment. The boiling points, molecular weight, structure and solubility parameters of the four solvents and that of the polyester are reproduced in Table 3.

**Table 3: Boiling Points, Molecular Weights, Solubility Parameters and Structures of the four Chlorinated Solvents.**

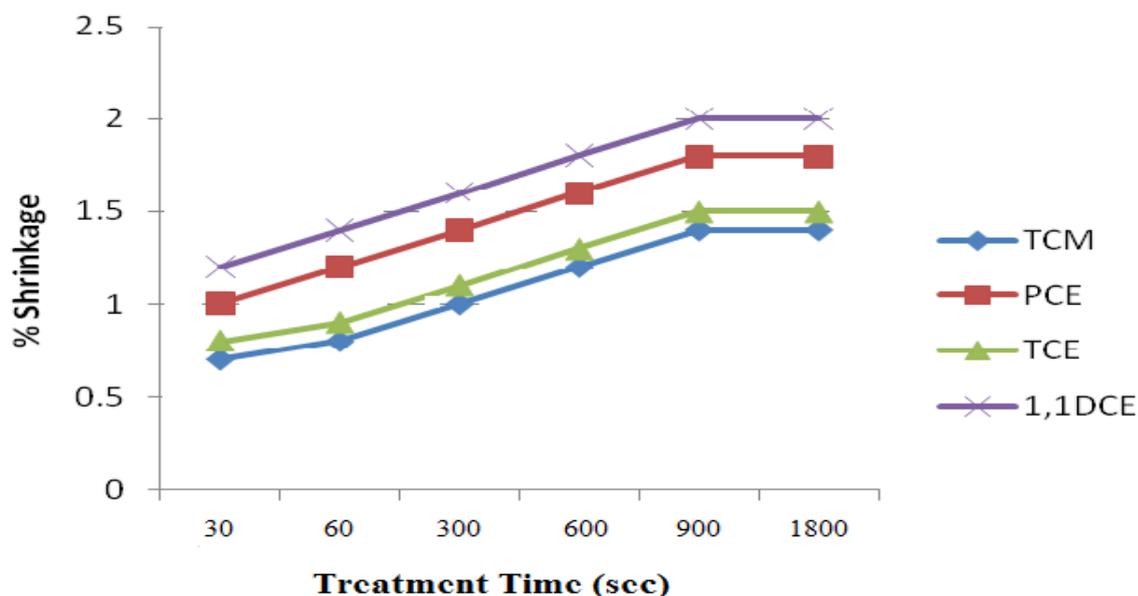
Solvent	B. pt (°C)	Mol. Wt. (g/mol)	Sol. Parameter(δ)	Structure
TCM	76.7	166	8.65	$\begin{array}{c} \text{Cl} \\   \\ \text{Cl} - \text{C} - \text{Cl} \\   \\ \text{Cl} \end{array}$
PCE	121	154	9.30	$\begin{array}{c} \text{Cl} \quad \quad \quad \text{Cl} \\ \diagdown \quad \quad \diagup \\ \quad \quad \text{C} = \text{C} \\ \diagup \quad \quad \diagdown \\ \text{Cl} \quad \quad \quad \text{Cl} \end{array}$
TCE	86.9	131.5	9.28	$\begin{array}{c} \text{Cl} \quad \quad \quad \text{Cl} \\ \diagdown \quad \quad \diagup \\ \quad \quad \text{C} = \text{C} \\ \diagup \quad \quad \diagdown \\ \text{H} \quad \quad \quad \text{Cl} \end{array}$
1,1-DCE	31	97	9.76	$\begin{array}{c} \text{H} \quad \quad \quad \text{Cl} \\ \diagdown \quad \quad \diagup \\ \quad \quad \text{C} = \text{C} \\ \diagup \quad \quad \diagdown \\ \text{H} \quad \quad \quad \text{Cl} \end{array}$

PET

10.70



**Fig. 1:** Structure of PET Fibre.



**Fig. 2:** Showing the Treatment time and Shrinkage (%) of the Fibre in the Chlorinated Solvents.

Figure 2, revealed a rapid increase in the percentage shrinkage values of the solvent treated fibres with increase in treatment time over a period of 900 secs before equilibrium shrinkage was achieved. This showed that shrinkage is time dependent.

From the values of the boiling points, molecular weights, solubility parameters and molecular structures of both the solvents and the polymer shown above, the overriding factors responsible for the trend in the shrinkage values observed are quite evident.

### 3.2.1 Molecular weights of the solvents.

From the perspectives of the molecular weights of the various solvents used, the order is that 1,1-DCE < TCE < PCE < TCM. In other words, the expected trend of solvent diffusion capacity into the polyester should be 1,1-DCE to be faster than TCE, then PCE and TCM in that order. As this will also reflect the ability of the solvents to penetrate the amorphous regions thereby affecting the overall morphology of the polymer i.e shrinkage and crystallization, then the amount of shrinkage caused should strictly follow that order. The result obtained did not actually follow this trend as the highest shrinkage value were caused by 1,1-DCE > PCE > TCE and TCM in that order with PCE swapping position with TCE to obliterate the observed order of their respective molecular weights. While it may be argued that this observation follows an expected order with anomalous behaviour from PCE, it is difficult to infer that, factors other than molecular weights of the solvents are not at play in deciding the shrinkage capacity of the polymer.

### 3.2.2 Boiling points of the Solvents

The ability of liquids to vaporize and diffuse into polymer matrix and penetrate the amorphous phase will depend on the heat of vapourization and by implication the forces of attraction holding the liquids together.

The heat of vapourization of a liquid is a useful quantity because it allows the calculation of the vapour pressure of the liquid at any temperature [8,9]. Thus, the boiling points of the respective solvents hold a crucial key to this observation. The lowest boiling point liquid here being 1,1-DCE is expected to agree to this rule as it has a boiling point of 31<sup>0</sup>C and this also displays the highest shrinkage in line with the observed trend. However, the remaining liquids in their respective order of boiling points are TCM (76.7<sup>0</sup>C), TCE (86.9<sup>0</sup>C) and PCE (121<sup>0</sup>C). Expectedly, given this order, the shrinkage values will be expected to follow in the order of 1, 1-DCE > TCM > TCE and PCE which again is seen to negate the observed trend.

### 3.2.3 Solubility parameter of the polymer and the solvents

The solubility parameters of the liquids used against that of the polymer are shown in Table 3. The solubility parameter concept defines the ability of the polymer/liquid to interact on the basis of similar forces of attraction operating between them. It also provides a numerical estimate of the degree of interaction between materials and can be good indications of solubility, particularly for non polar materials such as polymers [10].

Looking at the distribution of chemical bonds in the polymer and the solvents, a unique trend becomes discernible which could unlock the explanation for the observed results of the shrinkage experiments. The structure of the polymer consists of a flexible *ethyleneic* residue with saturated  $\sigma$  -bonds sandwiched by a rigid benzene ring with resonating conjugated double bonds flanked by two -COO- residues all having both  $\sigma$  and  $\pi$  bonds. Considering the structures of the four (4) solvents, one finds that 1,1-DCE, PCE and TCE also share similar bond structures as they all contain unsaturated C=C carrying  $\pi$  bonds within the molecules in addition to C-C  $\sigma$  and C-Cl and C-H  $\sigma$  bonds. Thus, similar forces of attraction varying only in degrees arising from slight differences in their polarities do operate in their structures. It is not surprising, therefore, that the solubility parameters of the three (3) solvents are within close range of one another and also closer to that of the polymer (10.7) compared to the distant value of 8.65 for TCM. What therefore, distinguishes them from one another, is the value of their respective solubility parameters which are  $\delta = 9.76$  for 1,1-DCE, 9.30 for PCE, 9.28 for TCE and 8.65 for TCM in relation to the 10.7 value for the polymer.

Since the observed trend of the shrinkage values follow the trend of the solubility parameters, it is safe to infer that the most important factor that has influenced the shrinkage of the polymer in the various liquids is, therefore, that of solubility parameter.

### 3.2.4 Effect on dimensional stability of the fibre

One of the core objectives for assessing the level of shrinkages caused by the chlorinated solvents on the polyester is to evaluate such effects on the dimensional stability of the polymer since this is very crucial to the laundry industry. To obtain the best results from laundry operations, liquids with the minimum harmful effects on the structures and aesthetics of the fabrics in addition to giving the best cleaning services are to be preferred. From the results obtained from the shrinkage values, 1,1-DCE, PCE, TCE and TCM have equilibrium shrinkage values of 40%, 36%, 30% and 28% respectively on the dimensional change of polyester fibre. Consequently, the best among the four solvents in terms of effecting minimal changes on the structure and quality of the fabric during laundry was found to be tetrachloromethane (TCM).

## IV. Conclusion

The results of this research work have been able to provide a basis upon which textile development in non-aqueous processing and finishing may be based.

#### **Acknowledgement**

The contributions of Messers Abe Taiwo, Jabar J.O., Akinola Kayode Federick, Ohalete Nnamdi Martins and Adeakin Olanibugbe (FUT, Akure) are gratefully appreciated.

#### **References**

- [1] [www.indiantextilejournal.com](http://www.indiantextilejournal.com)
- [2] Ugbolue, S.C.O. and Popoola, A.V., Studies on Solvent Induced Structural Modification of Poly (ethylene terephthalate) Filament. *Acta Polymerica* 40. Nr 7 (1989): 475-479.
- [3] Knox, B.H., Weigmann, H.D. and Scott, M.G., *Text. Res. J.* 45 (1975): 203.
- [4] [www.nonwovens.com](http://www.nonwovens.com)
- [5] Walters, J.P. and Buchanan, D.R., Glass Transition Temperatures of Polyamide Textile Fibres. Part II: Relationships between Tg and Dyeability. *Textile Research Journal*, 47 (1977): 451-456.
- [6] Popoola, A.V., Ph.D Thesis, Polymer Science and Technology Department, UMIST, (1983) Manchester, England.
- [7] Weigmann, H.D., Scott, M.C. and Rebenfeld, L., *Text. Res. J.* 43 (1973): 316.
- [8] Garai, J., Physical Model for Vaporization. *Fluid Phase Equilibra.* 283 (2009): 77-89.
- [9] Ge, X. and Wang, X., Calculation of Freezing Point, Depression Point Elevation and Vaporization Enthalpies of Electrolyte Solution by Modified Three-Characteristics Parameter. *J. Sol. Chem.*, 38 (2009): 1097-1117.
- [10] Kwok, A.Y., Greg, G.Q. and David, H.S., Synthetic Hydrogels 3: Solvent Effects on Poly (2-hydroxyethyl methacrylate). *Network Polymer* 45 (2004): 4017-4027.