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## Chemical and Physical Treatment of Poly (Ethylene Terephthalate) (PET) Fibre and Its Characterization

**Dr. Ohalete, Martins Nnamdi**

Post Doctoral Research Fellow, Department of Chemistry,  
Federal University of Technology, Akure, Ondo State, Nigeria

**Popoola, Adeola Victor**

Professor, Department of Chemistry,  
Federal University of Technology, Akure, Ondo State, Nigeria

**Adetuyi, A.O.**

Professor, Department of Chemistry,  
Federal University of Technology, Akure, Ondo state, Nigeria

### **Abstract:**

*The effect of heat and solvent treatments on the chemical degradation of the polyester fibres was investigated and their effects inducing structural and properties changes were thoroughly reviewed. Drawn poly( ethylene terephthalate) fibres (D.R. 5:1) were treated relaxed and tensed in dimethylformamide (DMF) and benzaldehyde at 95°C for varying periods of time. The PET fibres were also pre-crystallized at 160°C, 180°C and 200°C for 1 min., 1 h and 3 h, using dry hot air prior to liquid treatment study at 95°C and retention at 60°C. Thus resulting in a linear increase in the amount of liquid retained in the polymer as a function of time until equilibrium was attained. Specific functional groups were introduced on the surface of the untreated and pretreated polymer samples through aminolysis with primary amines such as methylamine, propyl amine and ethylamine; also polymer samples were treated with ethanol and water. Chemical reaction of PET with primary amines resulted in chain degradation and molecular weight lowering of the polymer. On complete degradation, the corresponding amide of terephthalic acid was obtained.*

**Keywords:** Aminolysis imbibition, liquid – induced crystallization, orientation

### **1. Introduction**

Polyester (PET) fibres found immediate acceptance in easy-care, wash-and-wear and durable press garments. They are widely used in apparel sector because of their unique physical properties such as good strength, drape, abrasion resistance and crease/wrinkle recovery in either wet or dry condition. In recent years, micro denier polyester fibres occupy major share in fashionable outerwear, functional sportswear and other home furnishings. Matsui, M. (2000), Mukhopadhyay, S. (2002). Wide variety of modified polyester fibres like anionic and cationic dyeable polyester fibres, flame-resistant fibres, antistatic fibres and hydrophilic fibres have also been developed for specific end uses. Datye, K. Y., Yaidya, A.A. (1984). Amorphous, un-oriented PET is of little commercial interest because of its poor mechanical properties, higher gas permeation, lower dimensional stability and higher extensibility. The physical and mechanical properties of PET, however, can be significantly improved by changing the crystallization rate, extent of crystallinity and orientation.

Heat and Chemical treatments of PET with different solvents such as dimethyl formamide (DMF), benzaldehyde and in primary and secondary amines and ethanol bring about changes in the fine structure, improvement in some important properties like dyeability and wettability of polymers Kopnick et al (2005). Polymeric fibers are manufactured into all sorts of daily as well as industrial goods. Fourné, F. (1995), Gries T, Sattler H (2005) and Engelhardt, A. (2011). The most prominent materials are thermoplastic among which poly (ethylene terephthalate) (PET), polyamides (PA) and polypropylene (PP) make up largest fraction. Wulfhorst, B., Gries, T., Veit, D. (2006), Walter et al (2010). Other thermoplastic polymers such as poly (vinylidene fluoride) (PVDF), belong to niche markets with highly specialized applications. Walter et al (2012).

The linear homopolymer poly (ethylene terephthalate) is the dominant composition for polyester fibres. Number average molecular weights of about 15,000 are required for useful textile-fibre properties, but lower values give staple of low tendency to pilling and higher values provide high strength fibres for industrial use.

Other desirable properties of PET (clear, lightweight, high strength, stiffness, favorable creep characteristics, low flavor absorption, high chemical resistance, barrier properties and low price) make it the material of choice for carbonated

soft drinks containers, fibers and films. Lyu, M. Y., and Pae, Y. (2003). Due to low cost, better aesthetic appearance, and better handling, PET is being preferred over polycarbonate (PC) polymers. Vander, G. N. (1999).

Polyethylene terephthalate (PET) is the material most commonly used to make the clear plastic bottles in which bottled water is sold. PET bottles are also in widespread use as containers for soda beverages, sports drinks, and condiments such as vinegar and salad dressing. PET bottles are also commonly used for the packaging of cosmetic products, such as shampoo, particularly when such products are sold in clear plastic bottles.

The potential of plastic packaging to introduce endocrine disruptors into foods and beverages has gone largely unrecognized until quite recently. Muncke, J. (2009). The plastics industry generally asserts that PET bottles are not a source of endocrine disruptors (American Chemistry Council).

Polyethylene terephthalate (PET, commonly known as polyester) fibres, are the most widely produced synthetic organic fibres and together with polyamide (nylon) fibres, make up the great majority of synthetic fibres produced. Davies, P. Francois, M., Grosjean, F. (2002).

The synthesis of PET begins with the esterification of either terephthalic acid or dimethyl terephthalate with ethylene glycol, yielding bis (hydroxyethyl) terephthalate (BHET). The BHET is then polymerized up to about 30 repeat units. Awaja, F., Pavel, D. (2005). Next, to achieve a degree of polymerization (DP), of about 100 repeat units, polycondensation is performed at temperatures > 270°C and pressures > 50 Pa. Ravindranath, K., Mashelkar, R. A. (1986). To produce bottle-grade PET, the DP must be >150 repeat units, which is typically accomplished via solid-state polymerization; a process that requires temperatures >200°C, pressures >100 Pa, and incubation times of at least 15 h. Al-Ghatta H, Cobrar S, Severini T. (1997).

The nature of polyester as regards some of the physical and chemical properties of the fibre has limiting effects on the variety of application to which the product fibre could be put to use. To achieve maximum utility and applications there is the need to modify polyester in order to overcome some of the major draw backs which include low moisture regain, static electricity or static charges build up, soiling problem, hydrophobic nature, tendency to pill, and lack of dye receptor sites in the polymer chain. Other drawbacks are pilling problem and difficulty in dyeing. By lowering the pilling nature, the garment made from PET fibres will retain elegant appearance for a long time. These low pilling fibres have lower tenacity than normal polyester fibres. Thus, although pills are formed in these fabrics, the pills are removed by simple brushing or washing. The research provides the method of modifying polyester fibres by inducement of crystallinity through heat and chemical treatments and shows how the treatments affect the response of polymer to degradation by organic liquids.

## 2. Materials / Methodology

The two organic solvents used were dimethylformamide (DMF) and benzaldehyde. The degradation solvents used were methylamine, ethyl amine, propyl amine, ethanol and natural water which serves as a control solvent. Other chemical solvents were standard reagents from BDH and of analytical grades.

### 2.1. Purification of the Fibre

The fibre was purified by refluxing in a soxhlet extractor at 60°C for 1 hour using petroleum ether. This was followed by vacuum drying at the same temperature for 24 hours. It was then scoured in 1gm per litre aqueous solution of Lissapol N, a non-ionic dispersing agent for 1 hour at 60°C, rinsed in distilled water and dried at 60°C for a further period of 24 hours in a desiccator with silica gel, prior to use.

### 2.2. Crystallization/Liquid Retention Studies of Pet Using Organic Liquids

Crystallization study of PET fibre samples was carried out in the presence of organic liquids (DMF and Benzaldehyde) at 95°C for various times ranging from 30 sec. to 1 h. For this purpose, DMF (dimethylformamide) and benzaldehyde were used. The samples which were mounted on stainless steel holders (H). Fig. (1), were contained in orifices through the chromium plated brass disc (G). The treatment bath itself was a 2 liter culture flask (D) containing the appropriate liquid (I) into which was inserted a thermometer and a variable high speed stirrer (E). The set up was contained in a water bath maintained at the temperature of treatment. The culture flask was fitted to a water cooled Liebig condenser (A), which was in turn connected to a cold running tap.

After each treatment, the sample was blotted dry of surface liquids, pressed under load and dried in a vacuum oven at 60°C / 15 mmHg for 3 h. They were then readied for X-ray, SEM, and IR analyses.

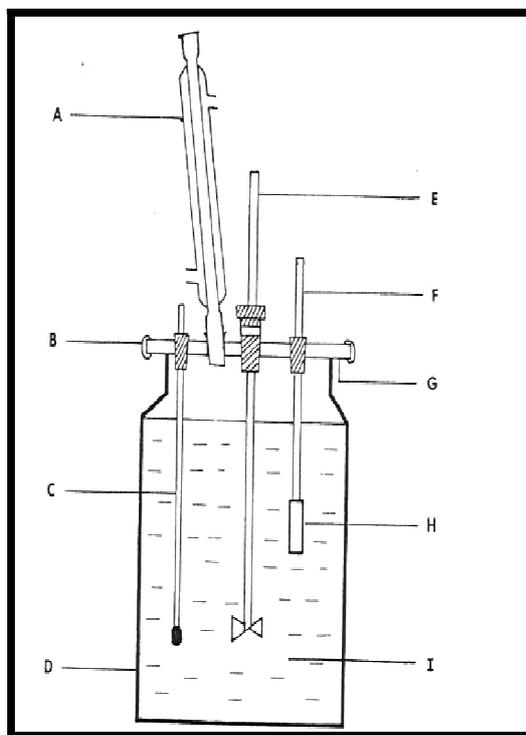


Figure 1: Liquid Crystallization and Retention Bath

- A – a water-cooled condenser
- B – a steel clip
- C – a thermometer
- D – a 2-litre culture vessel
- E – a variable high-speed stirrer
- F – a steel stick
- G – a chromium-plated brass disc
- H – a steel frame (for holding film samples) I – Liquid

### 2.3. Heat Setting of Pet Fibres

Heat setting treatment was carried out on the fibre to investigate the effect of the thermal annealing on the molecular structures of the polymer. The fibre was heat-set at 160°C, 180°C and 200°C, under relaxed conditions in dry heat. This experiment was carried out in a vapour bath apparatus Fig. (2); using an organic liquid with appropriate boiling range to the desired heat setting temperature. The apparatus or set-up was heated using an isothermal heating mantle. The heat stabilization treatments were carried out between 30 seconds to 3 hour. The set-up consists of a stoppered tube containing a thermometer which was inserted into the extended neck of a flask containing boiling organic solvent. With the temperature stabilized at 160°C, the stopper was quickly removed, the fibres suspended on a length of stainless steel wire were introduced and the stopper reinserted. Treated samples were withdrawn at intervals of 1 minute, 30 minutes and 3 hours. The whole process was repeated at stabilized temperatures of 180°C and 200 °C. Then the resulting samples were then dried for 24 h in an oven at 60°C; then cooled in desiccators. The samples were then stored prior for further analysis using Scanning Electron Microscope (SEM), X-ray diffraction test (XRD), solution viscosity, critical dissolution and mechanical properties determined using Instron tensile testing machine. The apparatus consist essentially of an outer round bottom liquid containing cup which is projected with a cylindrical jacket (C) which is connected to the jacket by means of a flash head reducer (D). Provision is made for an inner Pyrex-glass tube (A) which is suspended through a quick-fit neck into the vapour bath of the outer jacket. The former is closed using a woody cork (stopper) (F) bearing a 40cm long flexible wire which holds the thermometer (G) and (E) a small clip on which the fibre is suspended..

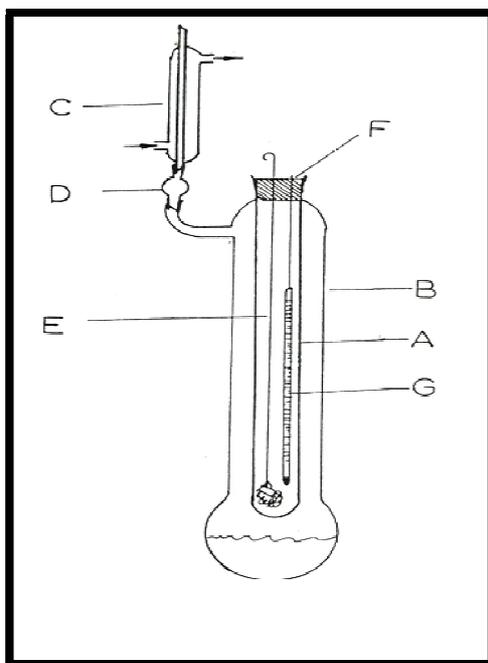


Figure 2: Heat – Setting Apparatus

#### 2.4. Weight Uptake / Liquid Retention Study.

Liquid retention at 60°C on the other hand was determined by gravimetric method. Samples used for this purpose were heated under vacuum for a period of 24 hours at 60°C. They were then transferred to a desiccator containing silica gel for a further period of 24 h. This was done to eliminate the effect that the presence of moisture that may be present in the polymer may have on the result obtained for the liquid retention.

Following the initial drying process, the samples (untreated/control and heat-set) were weighed and treated as described above at 95°C; dried over night at 60°C to achieve constancy of weight. They were again weighed on cooling and the constancy of the weight was ensured by returning them to the drying chamber and retaking the weights on cooling following a further drying period of 3 hours. An overnight drying time of between 15-24 hours was, however, found to achieve such constancy of weight.

The difference in the weight of the PET samples before and after treatment in the liquids followed by drying to constant weight was used to calculate the amount of liquid retained by the polymer at 60°C/15mmHg using equation (1):

$$\text{Liquid retention, molKg}^{-1} = \frac{W_t - W_{t0}}{W_{t0}} \times MW_{liq} \times 10^{-3} \quad (1)$$

All weights were expressed in milligrams  $W_t$ ,  $W_{t0}$ , are weights of treated and untreated PET respectively. The amount of t

#### 2.5. Amine Treatment (Aminolysis)

30 mg of the fibre was placed in an air tight tube containing 3.0 mL of 40% aqueous methylamine. After the degradation time, the samples were filtered under suction, carefully washed with distilled water and vacuum dried as 60°C for three hours. Following the cooling of the samples, they were reweighed and the degree of accessible and inaccessible regions within the polymer was deduced from the graph of weight loss as a function of degradation time. The experiment was repeated using other degrading agents as: propylamine, ethylamine, ethanol and natural water.

#### 2.6. Surface Characterization of the Degraded Polymer

The scanning electron microscope was used to examine untreated PET fibre sample (control) and sample treated with methylamine at room temperature for 24hrs. The resulting micrograph is presented in Fig. 3 and 4. The surface features resulting from the degradation; as well as the relative magnitude of the chemical 'etching' occurring, vary with the pretreatments which the fibres had undergone. The micrographs were taken at 5000X magnification, while the corresponding particle size distribution was obtained with IMAJEJ Software. The micrograph of the untreated PET was used to compare those of other treated PET fibrous strands with average particle size distribution from 450µm – 550µm, with the average particle size distribution of 500µm in more abundance. This indicates that a strand of polyester fibre contains different particle sizes. Other PET fibre samples were treated in other solvents such as ethylamine, propylamine, ethanol and water.

#### 2.7. Infra – Red (IR) Spectra of Undegraded and amine degraded PET

Untreated PET fibre samples and samples treated in methylamine and other solvent (ethylamine, propylamine, ethanol and water), at room temperature for 24 hours; were examined using FTIR. The resulting spectra are shown in Fig. 5 and 6. Notable peaks observed from the spectra were presented as shown in TABLE 1

## 2.8. Wide Angle X-Ray Diffraction Study

X-ray scattering diffraction were used for the untreated and treated samples. The crystallite size were calculated from its relationship with peak width at half maximum and the crystallinity content was individually calculated from amorphous content. First, amorphous content of the samples (A in %), will be determined from respective diffractograms by evaluating the integrated scattering intensities. Then the crystalline content (percentage crystallinity) was determined as (100A). The estimation of the crystalline content in the polymer samples involves a comparison of the relative intensity of the crystalline and amorphous region of the polymers, with the implicit assumption that the scattering powers of the two regions are equivalent and considering equal masses of scattering materials. The slight differences in the peak positions, intensity and diffused scattering maxima could be associated with the structural differences of the samples used in this study.

The d – spacing of the crystalline part of the polymer was calculated using equation (2), the Bragg equation:

$$n\lambda = 2d\sin\theta \quad (2)$$

Equation (3), Bragg spacing:  $d = \frac{n\lambda}{2\sin\theta}$  (3)

Where n is order of reflection (n = 1), d is Bragg spacing and  $\theta$  is Bragg's angle,  $\lambda$  is wavelength of radiation (1.542Å). The width ' $\Delta w$ ' at half the maximum of crystalline peak was measured and the crystallite size calculated using equation (4), the Scherer equation:

$$t = \frac{0.9\lambda}{\Delta w \cdot \cos\theta} \quad (4)$$

Where t is crystallite size and  $\Delta w$  is peak width at half maxima in radians; as shown in equation (5):

$$\Delta w = \frac{\phi_1 - \phi_2}{2} \quad (5)$$

Crystallinity values were calculated from diffraction area with the aid of equation (6):

$$\% \text{ Crystallinity} = \frac{1c}{1c+1a} \times 100 \% \quad (6)$$

Where 1a and 1c are diffraction intensities from amorphous background and crystalline centre respectively. Also crystallinity values were obtained from Critical Dissolution Time (CDT) data.

The correlation between the results obtained for both CDT and diffraction intensities showed that there was an increase in the diffraction peak intensity with increase in CDT values (crystallinity) of the fibres occurred.

## 2.9. Determination of Critical Dissolution Time (CDT) of the Treated and Control PET Filaments in 100% Phenol

The CDT of untreated control fibre, heat set and liquid treated samples were measured in 100% phenol at 60 °C. PET filaments prepared from the above samples were hung one at a time from a stainless spring which was attached to a wood – cork stopper. The yarn was suspended in phenol contained in a long transparent Pyrex tube 6 inches long and 1 inch diameter, filled with 100% phenol by means of a constant load of  $6.6 \times 10^{-2}$ gm. This was done in order to determine the time the PET fibre will break under the attached weight. The tube was immersed a water bath preset at 60 °C. The time needed from suspension of the yarn in phenol till the falling off of the attached weight was recorded using a stop watch. For each sample, 5 determinations were made and the mean value taken as the critical dissolution time.

### 2.9.1 Percentage Crystallinity from CDT Values

The apparent crystallinity values were obtained from the CDT data using equation (7):

$$\% \text{ Crystallinity} = \frac{CDT_{treated} - CDT_{untreated}}{CDT_{treated}} \quad (7)$$

where,  $CDT_{treated}$  = Critical Dissolution Time of treated fibre.

$CDT_{untreated}$  = Critical Dissolution Time of control fibre.

The equation worked perfectly under the following assumptions;

- That the annealed fibres consist essentially of two phases i.e. Impermeable crystallites embedded within the amorphous matrix;
- On immersion of the fibre in the solvent, there is complete penetration of the solvent molecules through the amorphous regions and that each crystal plane of the embedded crystallites experiences the same concentration of the solvent; and
- The amorphous matrix is dissolved completely prior to the crystalline region.

### 3. Results and Discussion

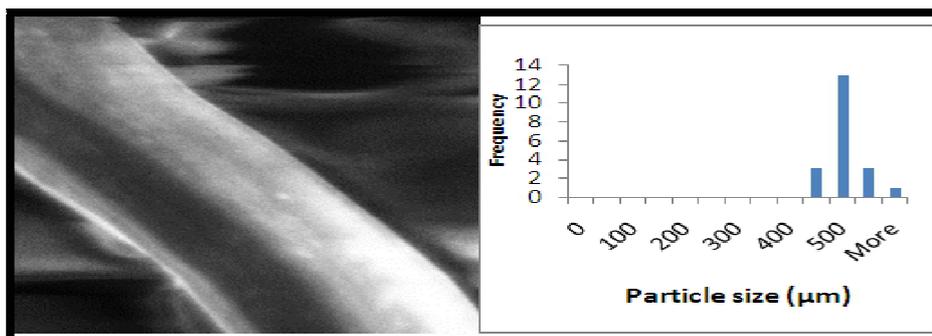


Figure 3: SEM Micrograph and Particle Size Distribution of Untreated PET

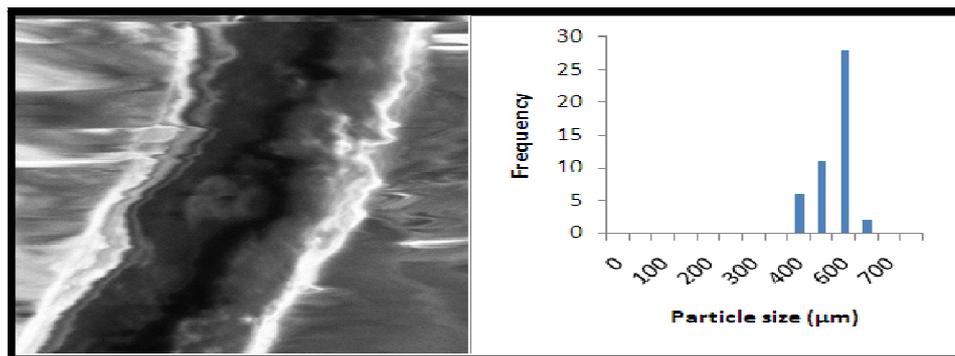


Figure 4: SEM Micrograph and Particle Size of Methylamine Treated PET For 24 H

It is evident from the SEM micrographs in Fig. 3 and 4, that both the mode of attack of polyester by the amine and the ease of penetration into the PET structure by the degrading liquid, was enhanced by the thermal and liquid pre-treatments of the fibre prior to degradation.

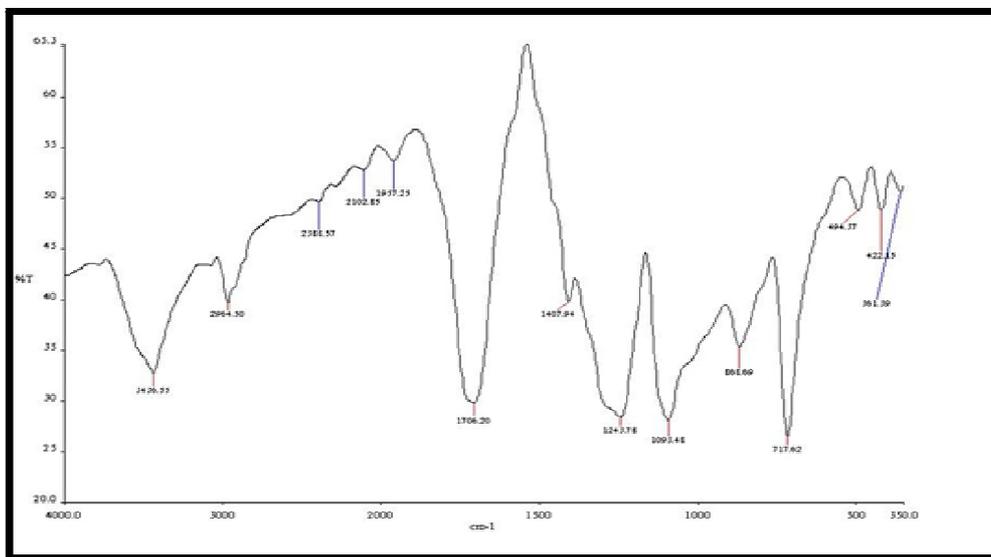


Figure 5: FTIR Spectrum of Control Sample

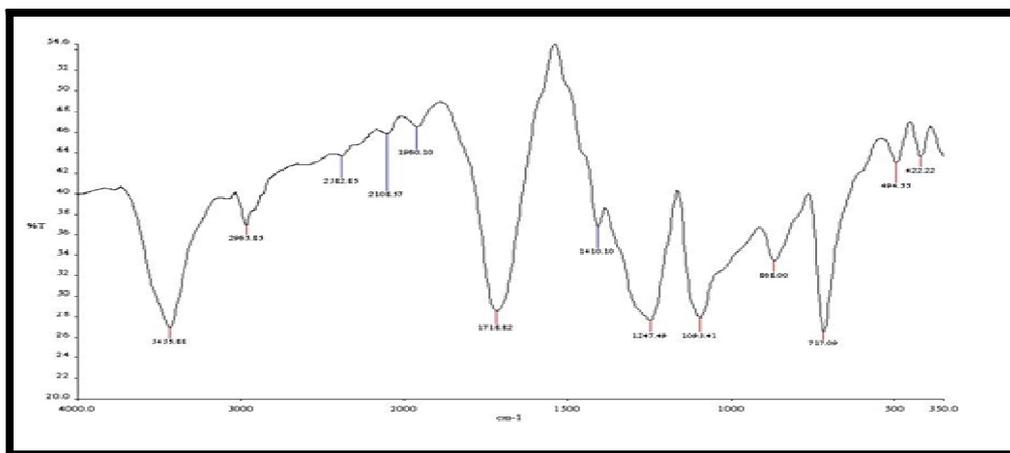


Figure 6: FTIR Spectrum of Methylamine Treated PET for 24 H

It is clearly seen from these spectra that the spectral changes with time of aminolysis are similar for all samples. There is a fundamental difference between the IR spectra of the undegraded and the completely degraded PET in that there is C = O absorption band at 1720cm<sup>-1</sup> which is characteristic of an ester bond; its disappearance on complete degradation and replacement by a primary amide = N – 4 bond at 3350cm<sup>-1</sup> is a clear manifestation of the aminolysis action on the fibre. The stretching vibrations ν(C=O) of the ester structure of polyethylene terephthalate is localized at 1712cm<sup>-1</sup> and in fact is an envelope of several bands belonging to the carbonyl group.

Wavenumber (cm <sup>-1</sup> )	PET Fibre Treated With					
	Control	Water (24 h)	Ethanol (24 h)	Ethylamine (24 h)	Propylamine (24 h)	Methylamine (24 h)
OH-stretch	3436.55	3433.56	3434.27	3436.14	3434.14	3435.88
C–H stretch	2964.50	2965.71	2965.64	2966.75	2967.09	2965.85
C=O stretch	1706.20	1706.21	1710.53	1728.09	1718.53	1718.82
C–C stretch (in-ring)	1407.94	1458.54	1452.84	1452.84	1407.25	1410.10
C–H wag	1243.78	1244.32	1244.76	1283.00	1244.17	1247.49
C–N stretch	-	-	-	1082.66	1092.45	1095.41
N–H wag	-	-	-	865.80	866.66	868.00

Table 1: Functional Groups Observed from FTIR Spectra of PET Fibres

Reagent	Water Treated PET Fibre	Crystallites Size	Degree of Crystallization
Water	Untreated	25.63	54.66
	Water Treated 2h	15.57	40.38
	Water Treated 24 h	13.73	40.94
Ethanol	Untreated	25.63	54.66
	Ethanol Treated 2 h	16.42	58.15
	Ethanol Treated 24 h	15.07	44.23
Ethylamine	Untreated	25.63	54.66
	Ethylamine Treated 2 h	13.63	46.75
	Ethylamine Treated 24 h	11.67	40.99
Propylamine	Untreated	25.63	54.66
	Propylamine Treated 2 h	19.70	48.87
	Propylamine Treated 24 h	16.27	39.69
Methylamine	Untreated	25.63	54.66
	Methylamine Treated 2 h	14.08	55.37
	Methylamine Treated 24 h	14.44	56.20

Table 2: XRD Data for Untreated and Chemically Treated Fibres at Room Temperature for 2h and 24 H

Water Treated PET Fibre	Crystallites Size	Degree of Crystallization
Untreated	25.63	54.66
Heat Treated (160 <sup>o</sup> C) 1hours	13.67	45.08
Heat Treated (160 <sup>o</sup> C) 3hours	13.44	37.87
Untreated	25.63	54.66
Heat Treated (180 <sup>o</sup> C) 3hours	17.25	54.14
Heat Treated (180 <sup>o</sup> C) 1hours	16.86	49.45

Table 3: XRD Data for Untreated and Chemically Treated Fibres at Different Temperature

As presented in Tables 2 and 3 it is seen that there was rapid development of Crystallinity following both thermal and liquid treatments. However, Crystallinity developed more rapidly during the heat treatment than during the liquid treatment. Also the size of the Crystallites formed during the thermal treatment is bigger than the ones formed during liquid treatment.

#### 4 Conclusions

The values of the diameters of samples obtained from SEM study showed that there is slight reduction in the diameter of the PET fibre when treated with (methylamine, propylamine, ethylamine degrading solvents and ethanol). The wide angle X-ray scattering shows that there is decrease in crystallite size ( $t$ ) as evident from increase in the half width peaks ( $\Delta W$ ) in treated samples in comparison to the untreated samples. In addition, there is decrease in the percentage crystallinity ( $C$ ) and in the Bragg spacing ( $d$ ) in the above treated cases, which may be due to considerable destruction of crystallites. The findings obtained through SEM and XRD are consistent with each other. This conclusion confirms that polyester fibre is affected to some extent when treated in amines and alcohols. In essence the fibres degrade more in primary and secondary amines than in alcohols. This degradation introduces functional sites, which enhances the modification of the polyester for other end uses.

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