

# X-Ray Diffraction Studies for Identification of Polyethylene Terephthalate Fibres

Devi Singh<sup>1\*</sup>, Hitendra K. Malik<sup>2</sup>, Chinmay K. Gupta<sup>1</sup> and Varsha Singh<sup>3</sup>

<sup>1</sup>Department of Physics, Manav Rachna International University, National Capital Region, Aravali Hills, Sector-43, Faridabad – 121001, Haryana, India; drdevisingh.fet@mriu.edu.in, chinmay.fet@mriu.edu.in

<sup>2</sup>Department of Physics, Indian Institute of Technology, New Delhi - 110016, India; hkmalik@physics.iitd.ac.in

<sup>3</sup>Department of Electronics and Communication Engineering, Manav Rachna International University, National Capital Region, Aravali Hills, Sector-43, Faridabad - 121001, Haryana, India; varsha.fet@mriu.edu.in

## Abstract

**Objective:** Our main objective is to do X-ray diffraction (XRD) analysis of polyethylene terephthalate (PET) fibres obtained from different manufacturers in India. It is to determine whether this physical characteristic could be used in differentiating these fibres of one type or not. **Method:** X-ray diffraction patterns of the fibres of 8 samples were obtained using a Phillips PW 1840 X-ray Diffractometer. **Findings:** The results indicate that X-ray diffraction method may not provide definite clue to the identification of fibres, which are chemically similar but originating from different sources. However, more detailed studies are required in order to confirm the inappropriateness / appropriateness of the X-ray method. On the other hand, we have differentiated these fibres based on their tensile behaviour. **Applications:** The method has applications in forensic science investigations for identification and comparison of PET fibres.

**Keywords:** Degree of Crystallinity, Polyethylene Terephthalate (PET) Fibres, X-ray Diffraction (XRD)

## 1. Introduction

Now a days polymers are very important in our day to day life. They are made of large chains of monomers with degree of polymerization of one lakh or above<sup>1</sup>. Polymers have complexity in structure. The molecular chains arrange themselves in variety of ways, if they are arranged in ordered way, they form crystalline structure with three dimensional symmetry, else amorphous structure if randomly oriented. Variety of commercially available polymers like Polyethylene (PE), Polypropylene (PP), Nylon, Polyethylene Terephthalate (PET commonly known as polyester), polyacrylates are in demand. Synthetic polymers like PET, PP and nylon can be used as fibers also. This paper lay emphasis on PET. It was discovered in 1941 in the laboratories of the Calico Printers Association in Lancashire, England. They are considered to be most versatile of all modern synthetic fibres. PET

have wide range of properties and hence, many uses in different walk of life. Polyester makes up about 18% of world polymer production and is the fourth-most-produced polymer after polyethylene (PE), Polypropylene (PP) and Polyvinyl Chloride (PVC). They are highly compatible and easily blend with natural fibres. These fibres are, therefore, very extensively used in the manufacture of textiles besides having numerous uses. A polyester fiber is composed of linear macromolecules comprising at least 85% (by mass) of the chain of an ester of a diol and terephthalic acid. PET polymers contains weakly polar carbonyl groups and held together by van der Waals' forces having hydrophobic interactions. It is highly crystalline in nature (65-85%) and have good strength, with no loss of strength on wetting. It has low cost of production as compared to other polymeric fibers and can easily blend with staple fibers like cotton or wool, thus used as huge variety in garment industry and have other uses too.

\*Author for correspondence

In case of forensic science community, fibers are the most frequent encountered evidences found at the site of crime. This paper lays especial emphasis on the evidential value of textile fibres encountered in forensic science investigations<sup>2-4</sup>. Several methods have been used in the forensic science examination for the comparison of these fibres. For example, birefringence for differentiating fibres<sup>5</sup>, use of tensile behavior<sup>6-8</sup>, thermal analysis methods<sup>9</sup> and Raman micro spectroscopy<sup>10</sup> are very common. However a systematic approach in this direction is still desirable.

Many of the procedures used in forensic science identification and comparison of textile fibres are primarily concerned with the microscopical examination of physical morphology and optical properties of the fibres. Other methods are based on the instrumental analysis of textile fibres. In most cases these procedures will afford positive identification of the generic type of textile fibres and will enable the criminalist to determine whether or not the questioned fibres could have originated from the sources of known fibres. However this is not enough. Methods that are capable of detecting subtle differences between questioned and known specimens are needed so that a stronger opinion regarding commonality of origin can be rendered. This need is more apparent when fibres from different sources of same generic type that exhibit very similar physical characteristics and chemical properties are to be compared. Some efforts in this direction have been made where researchers have developed more sensitive procedures for the identification and comparison of textile fibres<sup>11,12</sup>. However, the problem is far from being solved. Therefore, a detailed and systematic effort in this direction is called for.

X-ray diffraction is one of the powerful physical techniques for investigating the atomic and molecular level structure of polymers in general and fibres, which forms the basis of all textiles, in particular<sup>13,14</sup>. X-ray diffraction patterns produced by textile fibres are a result of the characteristic crystalline structure of their basic chemical constituents and their special arrangement in the fibre. X-ray analysis is not only an important tool for investigating the crystalline structure as such, but it also provide valuable information about certain mechanical phenomena in fibres, e.g., unfolding of molecules during stretching reorientation and slippage of crystallites during elongation, chemical reactions, e.g., mercerization, formation of derivatives by topochemical reactions, and physico-chemical phenomena, e.g., swelling, hydration,

etc. X-ray analysis also allows the evaluation of degree of crystallinity, orientation of crystallite in fibres and their size, etc.

In the characterization of semi-crystalline fibres, the concept of degree of crystallinity is extremely useful. This is because a number of important characteristic of the fibres, e.g., their mechanical properties, dye-uptake, etc., have been found to be affected by their degree of crystallinity. The crystallinity of PET fibres has been studied extensively by employing x-ray diffraction techniques. For determining the crystallinity of polymeric materials from their x-ray diffraction pattern, several procedures have been suggested<sup>15</sup>. These methods have been evaluated by<sup>16</sup> in case of Polyethylene Terephthalate (PET) fibres. It has been concluded by them that the absolute crystallinity of a particular sample, as determined by these procedures, may show considerable variations. Determination of crystallinity of PET fibres has also been investigated by several other workers<sup>17,18</sup>.

The knowledge of molecular and crystalline structure of fibres is not only of interest as a mere structural (morphological) feature, but is also responsible for many of their physical and physico-chemical properties. It is, therefore, expected that x-ray diffraction can be employed for the identification of a fibre. The use of this method in the identification of different polymeric fibres has long been recognized as a non-destructive technique requiring small amount of sample. However, no serious efforts have been made to apply the x-ray diffraction method to the identification of fibres of same chemical structure but subjected to different physical and chemical treatments. In the present work, an attempt has, therefore, been made in this direction. Here this method has been employed to identify PET fibres originating from different sources.

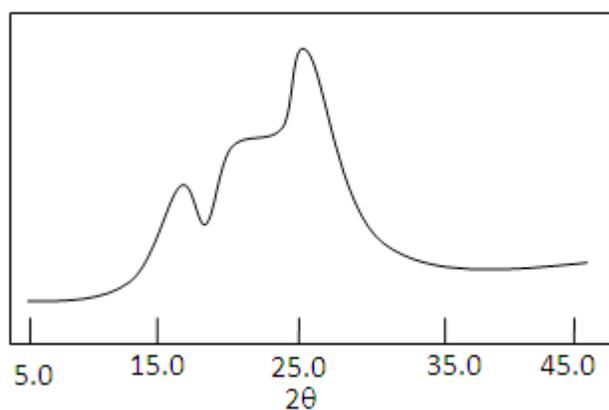
## 2. Materials and Method

The preparation and mounting of the specimen constitutes the most important experimental element in the X-ray analysis of polymeric fibres. In the present work eight PET fibre samples of varying denier and originating from different sources have been used. The fibres were cut into short strands and compacted in a rectangular aluminium die under nominal hand pressure. The compacted sample was then transferred to the sample holder. A Phillips PW 1840 X-ray Diffractometer was used for obtaining the X-ray diffractograms. The system was switched on and sufficient time was allowed to elapse for its stabilization.

The aluminium sample holder containing the sample was then mounted on the rotating stage of the Diffractometer. Nickel filtered  $\text{CuK}_\alpha$  radiations at 35 KV and 20 mA were employed. The counter was set for  $2\theta \approx 0^\circ$  and connected to a counting rate meter. The output of this circuit is fed to a fast acting automatic recorder, which derives a pen on the chart. The counter is then driven at a constant angular velocity through increasing value of  $2\theta$  until the whole angular range is scanned. At the same time, the paper chart on the recorder moves at a constant speed, so that the displacement along the length of the chart is proportional to  $2\theta$ . In the present work diffractogram of PET fibres were recorded at a scanning speed of  $2\theta \approx 1^\circ/\text{min}$  and a chart speed of 5mm/min. Diffractograms for completely amorphous standard was obtained from Department of Textile Technology, IIT Delhi. From the diffractograms, the peak positions and other information such as crystallinity were then obtained.

### 3. Results and Discussion

The diffractograms obtained for eight PET samples, investigated in the present work, have similar shapes. A typical diffractogram obtained in the present work for a PET fibre is shown in Figure 1. The general shape of this diffractogram is in agreement with the literature reported diffractograms of PET fibres.



**Figure 1.** A Typical X-ray Diffractogram for PET Fibre Sample.

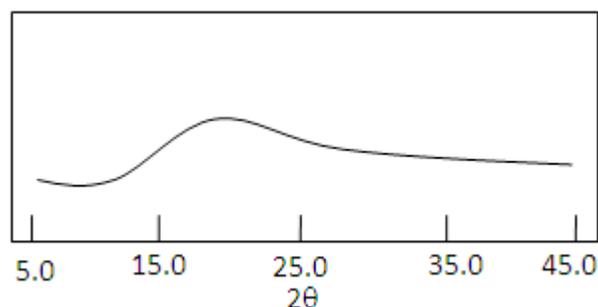
The diffractogram for the amorphous standard as obtained in the present work is shown in Figure 2.

The diffractogram shown in Figure 1 exhibit three characteristic peaks at  $18^\circ$ ,  $23.4^\circ$  and  $25.8^\circ$ . These correspond to (010) ( $1\bar{1}0$ ) and (100) reflections. The values

of diffraction angles corresponding to these reflections obtained for different PET fibre samples are given in Table 1. The crystallinities of these samples as determined by Farrow and Preston procedure, in which radial scans for the randomized sample and for the amorphous standard are required for calculation of percent crystallinity. The degree of crystallinity is given by

$$X = C / (C + A)$$

where X is degree of crystallinity (values are mentioned in Table 1), C is integrated area of the curve corresponding to the crystalline phase and A is area corresponding to the amorphous part.



**Figure 2.** A Typical X-ray Diffractogram for PET Amorphous Fibre Sample.

**Table 1.** Peak diffraction angles and crystallinities of PET fibre samples

S. No	Sample	Denier	$2\theta_1$	$2\theta_2$	$2\theta_3$	Crystallinity in %
1.	A	1.0	17.6	23.2	25.5	42
2.	B	2.0	18.0	23.0	25.4	50
3.	C	3.0	18.4	23.8	26.0	52
4.	D	1.0	18.0	23.4	25.8	49
5..	E	2.0	18.0	23.8	25.8	47
6.	F	2.0	18.0	23.4	26.0	49
7.	G	3.0	18.0	23.4	25.8	47
8.	H	3.0	17.8	23.4	25.8	47

The shapes of the x-ray diffractograms for eight samples were found to be similar. The peak angles (Table 1) for these samples, as determined from their respective diffractograms, were also found to be equal within experimental error. The samples investigated prominently exhibit (010) ( $1\bar{1}0$ ) and (100) reflections. This shows that basic crystal structure of the fibre samples is triclinic and is same for all of them. Thus the variations in the manufacturing process to which these samples were subjected perhaps do not affect the crystalline structure.

On comparing these samples in respect of their crystallinities, it is observed that the crystallinity of a sample is found to depend on its denier and its source of origin. This dependence, however, does not show any definite trend. As seen from Table 1, the crystallinity of three fibre sample A, B and C obtained from one source is found to increase with increasing denier while an opposite trend is observed for the fibre samples D and E obtained from another source. Again, on comparing the crystallinities of sample having same denier but procured from different sources, no definite trend appears to emerge. The crystallinity of a polymer sample can be modified by several physical processes. In the manufacturing of PET fibres, the raw material is subjected to large number of physical processes. Any variation in them could lead to changes in crystallinity of the end product. Therefore, absence of any definite trend in the samples investigated is not very surprising considering the number of variables involved in their production. Thus from the present investigation it appears that perhaps the X-ray diffraction method does not provide definite clue to the identification of fibres which are chemically similar but originating from different sources. As the crystallinity of a fibre sample is intimately related with its physical properties such as mechanical strength, PET fibres obtained from different sources and having different denier exhibits variation in their mechanical properties. On the basis of mechanical properties the identification of chemically similar fibres but originating from different sources is possible. Therefore before discarding X-ray diffraction method for such identification in forensic science perhaps the problem requires a detailed and careful consideration.

## 4. Conclusion

This paper presents X-ray diffraction technique for identification and comparison of PET fibres. The method can be employed for identification of chemically different fibres but it appears that perhaps the X-ray diffraction method does not provide definite clue to the identification of fibres which are chemically similar but originating from different sources. Based on the mechanical properties and birefringence the identification of chemically similar fibres but originating from different sources is possible, therefore before discarding X-ray diffraction method for such identification in forensic science perhaps the problem requires a detailed and careful consideration.

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