

## Analysis of microstress in neutron irradiated polyester fibre by X-ray diffraction technique

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**Abstract.** Microstresses developed in the crystallites of polymeric material due to irradiation of high-energy particle causes peak broadening and shifting of X-ray diffraction lines to lower angle. Neutron irradiation significantly changes the material properties by displacement of lattice atoms and the generation of helium and hydrogen by nuclear transmutation. Another important aspect of neutron irradiation is that the fast neutron can produce dense ionization at deep levels in the materials. The polyethylene terephthalate (PET) fibre of raw denier value, 78.2, were irradiated by fast neutron of energy, 4.44 MeV, at different fluences ranging from  $1 \times 10^9$  n/cm<sup>2</sup> to  $1 \times 10^{12}$  n/cm<sup>2</sup>. In the present work, the radiation heating microstresses developed in PET micro-crystallites was investigated applying X'Pert-MPD Philips Analytical X-ray diffractometer and the effects of microstresses in tensile strength of fibre measured by Instron have also been reported. The shift of 0.45 cm<sup>-1</sup> in the Raman peak position of 1614.65 cm<sup>-1</sup> to a higher value confirmed the development of microstresses due to neutron irradiation using micro-Raman technique. The defects due to irradiation were observed by SEM micrographs of single fibre for virgin and all irradiated samples.

**Keywords.** Microstress; PET; neutron fluences; XRD; SEM; micro-Raman technique.

### 1. Introduction

In general, the modification of polymer properties under ionizing radiation (Davenas *et al* 2002) is a subject of great interest due to the increasing uses of polymers in various fields. Among the varieties of synthetic fibres, polyethylene terephthalate (PET), also commonly known as polyester, is significant because of its high mechanical strength, inertness to chemical action and resistance to thermal environment. Again, PET fibres are mainly used in textile industry (Bhata and Naik 1984; Patel and Bal 2001). Apart from that, it is also used in the field of surgical polymeric textiles (Phaneuf *et al* 1997; Ferreira *et al* 2002; Metzger 2003), composites (Fu *et al* 2002), nanocomposites (Chang *et al* 2004), conducting polymer (Mishra *et al* 2000), electroactive polymer (Patel and Mallick 2000) etc. Polyesters are mainly cross-linked when irradiated (Kuleznev and Shershnev 1990). Then this irradiated polymer possesses improved tensile, increased rigidity, improved yield strength, higher melting temperature, decreased chemical solubility and swelling in the usual solvent etc (Alger 1965).

When fast neutron undergoes an interaction, it does so with a nucleus of the absorbing-material; as a result, the neutron may either totally be replaced by one or more

secondary radiation or produce significant changes in the energy or direction of the neutron. The secondary radiation results from above neutron interaction almost always produce heavy charge particles. The mechanism of the production of these heavy charge particles is either due to neutron-induced nuclear reaction or due to neutron collisions with nuclei of absorbing materials. As a result, materials gain enough energy; hence modification in the material properties takes place. In head-on collision with hydrogen or hydrogen like materials, the neutron transfers all its kinetic energy in a single encounter. The maximum kinetic energy of the recoil nucleus ( $E_R$ )<sub>max</sub> can be expressed by (Knoll 1989)

$$(E_R)_{\max} = \frac{4A}{(1+A)^2} E_n,$$

where  $A$  is the mass of the target nucleus per neutron mass and  $E_n$  the kinetic energy of incident neutron.

Since a polymer material consists of low  $Z$  elements like hydrogen, carbon etc neutron irradiation (Abou Taleb *et al* 1996; Srivastava and Virk 2000) significantly changes the material properties by the displacement of lattice atoms and the generation of helium and hydrogen by nuclear transmutation. Another important aspect is that, the fast neutron can produce dense ionization at deep levels in the material. Such an effect is difficult to be obtained by direct ionization radiation like protons, because it will only produce ionization at the spot, receiving radiation.

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The stress remaining in the crystallites after all external forces are removed or the treatment being completed is called residual stress or microstress. This microstress varies from one grain to another or one part of the grain to another part on a microscopic scale. If this stress is quite uniform over large distances, then it is called as macrostress. In general, if there is a residual tensile (positive) stress on the surface during fabrication or modification, that part will tend to fail more readily in service due to cracking, sapling, etc as compared to a residual compressive (negative) stress on the surface. Thus, it is important to ascertain the sign and magnitude of residual stress (Clark 1963).

X-ray diffraction method for determination of residual stress has the unique advantage over all other methods, because it can be used to measure these stresses non-destructively on surfaces. However, experimental measurement of residual micro-stresses in polymeric system (Young *et al* 1973; Balasingh and Singh 1997) is limited. Hence an attempt has been made in this investigation to study the neutron-induced microstress in polymer fibre applying X-ray diffraction.

## 2. Principle

The strains developed in the crystallites due to radiation heating or irradiation manifest as changes in the lattice planes, causing line shifting. These changes in the lattice planes are measured by the X-ray diffraction method. Microstress causes diffraction line broadening, while macrostress causes line shifting. The relation between the broadening produced and the nonuniformity of the strain can be verified by differentiating the Bragg law. The spacing,  $d$ , of a set of planes in a crystal is related to the Bragg angle,  $q$ , and the wavelength,  $\lambda$ , by the equation

$$d = \frac{\lambda}{2 \sin q} \quad (1)$$

The expression for change in  $d$  due to irradiation can be measured by noting the change in  $q$ .

Differentiating  $d$  with respect to  $q$ , we have

$$\begin{aligned} \frac{\Delta d}{\Delta q} &= -\frac{\lambda}{2} \operatorname{cosec} q \cdot \cot q \\ &= -d \cot q, \\ \text{or } \frac{\Delta d}{d} &= -\cot q \cdot \Delta q. \end{aligned} \quad (2)$$

Since diffraction angle is measured in terms of  $2q$ , then

$$\begin{aligned} \frac{\Delta d}{d} &= -\cot q \frac{\Delta 2q}{2} \\ \Rightarrow \Delta 2q &= -2 \frac{\Delta d}{d} \tan q. \end{aligned} \quad (3)$$

Hence,

$$b = \Delta 2q = -2 \frac{\Delta d}{d} \tan q, \quad (4)$$

where  $b$  is the extra broadening, over and above the instrumental breadth of the line due to a fractional variation in plane spacing  $\Delta d/d$ . The above (4) allows the variation in strain,  $\Delta d/d$  to be calculated from the observed broadening.

If  $d_u$  indicates the non-irradiated (unstressed) spacing and  $d_s$  the spacing in the irradiated (strained) fibre, the microstrain in the particles in the direction normal to the diffracting plane is

$$e = \frac{\Delta d}{d} = \left( \frac{d_s - d_u}{d_u} \right) \quad (5)$$

If  $d_s > d_u$ , then  $\Delta d/d$  is positive which indicates that the residual stress is tensile and if  $d_s < d_u$ , then  $\Delta d/d$  is negative indicating generation of residual compressive stress in the surface. This value of  $\Delta d/d$ , however, includes both tensile and compressive strains. Assuming both are equal for the micro-crystallites, the value of  $\Delta d/d$  must be divided by two (Cullity 1978) to obtain the maximum tensile strain alone, or maximum compressive strain alone. Again, maximum microstress present in the sample can be defined as

$$s_{\text{stress}} = \frac{e}{2} E. \quad (6)$$

Solving (5) and (6), we obtain

$$s_{\text{stress}} = \frac{1}{2} \frac{\Delta d}{d} E, \quad (7)$$

where  $E$  is the elastic constant or generally known as Young's modulus of the material.

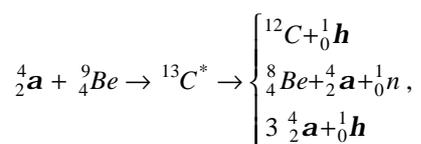
## 3. Experimental

### 3.1 PET fibres

Partially oriented yarn (POY) of polyethylene terephthalate (PET) fibre used for our investigation was obtained from a commercial polyester plant, which produces fibre through the following process. Esterification of purified terephthalic acid and ethylene glycol produces oligomer, which is subjected to polycondensation process via a 3-stage polycondensation reactor to produce viscous molten PET polymer material. The above hot molten polymer material is allowed to pass through a spinneret where it enters through very fine holes under various machine-setting parameters to produce long PET fibres or POY. The fibre used for the above irradiation study is of bright yarn type with raw denier (weight in gram of 9000 meter of yarn) value of 78.2.

### 3.2 Neutron source

The radioactive neutron source (Leo 1987; Knoll 1989) used in laboratory is mainly based on either spontaneous fission or on nuclear reactions. The latter is a more convenient method for producing neutrons. Nuclear reactions of (**a,h**) and (**g,h**) types occur with many nuclei with excited energy greater than the neutron binding energy, which can decay, to neutron emission; however, only those with the highest yield are used. Generally, such sources are made by mixing the target material like beryllium with a suitably strong **a** or **g** emitter. When bombarded by **a** particles, beryllium undergoes a number of reactions, which lead to the production of free neutrons (Leo 1987) as follows



where  ${}^{13}\mathbf{C}^*$  is the excited compound nucleus formed, which decays through a variety of ways depending on the excited energy. The dominant reaction, however, is the decay to  ${}^{12}\mathbf{C}$  or to the 4.44 MeV excited state of  ${}^{12}\mathbf{C}$ . The neutron radiation source used for the present irradiation study was produced from an Am-Be source by (**a, h**) type nuclear reaction. Taking  $\text{Am}^{241}$  as a **a**-source of energy (5.48 MeV), an experimental neutron yield of about 70 neutrons per  $10^6$  **a**'s is generally obtained from a beryllium target. A neutron beam of energy, 4.44 MeV and flux,  $2.2 \times 10^6$  n/cm<sup>2</sup>/s was used to irradiate samples in air at the atmospheric pressure in the temperature range 22–27°C for different exposure times to get three different i.e. II to IV, fluences ranging from  $1 \times 10^9$  n/cm<sup>2</sup> to  $1 \times 10^{12}$  n/cm<sup>2</sup> and are tabulated in table 1.

### 3.3 Sample preparation

Fibre sample was mounted on a special type of fibre sample holder (Kakudo and Kasai 1972) to form a flat sample of uniform length, breadth and thickness in each test sample for wide-angle X-ray diffraction (WAXD) study.

Stripes from the general-purpose brown paper of area  $80 \times 30$  mm<sup>2</sup> were taken. In the centre of the stripe a

$20 \times 20$  mm<sup>2</sup> patch was taken out. Fibre of length 80 mm was fixed at the centre of paper stripe with the help of suitable adhesive (Fevicol), which is non-reactive to the fibre. Again another paper stripe of the same type was fixed on the top of the fibre, so that the fibre lies in the centre of both the paper stripes and leave for proper drying. The well-fixed (dried) sample was loaded in-between two grips of the INSTRON. After proper setting of the sample, the sides of the paper tape was cut, so that the extra load required to break the paper with fibre sample can be detached.

### 3.4 Experimental techniques

The X-ray diffraction data was collected using a Philips Analytical X-ray Instrument, X'Pert-MPD (PW 3020 vertical goniometer and PW 3710 MPD control unit) employing Bragg–Brentano parafocusing optics. The XRD patterns were recorded with a step size of 0.01° on a 3–50° range with a scanning rate of 2°/min. Line focus Ni-filtered  $\text{CuK}_\alpha$ -radiation from an X-ray tube (operated at 40 kV and 30 mA) was collimated through soller slit (SS) of 0.04 rad., fixed divergence slit of 1° and mask (5 mm) before getting it diffracted from the sample. Then the diffracted beam from the sample was well collimated by passing it through a programmable anti-scattering slit of 1° to reduce air scattering, programmable receiving slit of 0.3 mm and soller slit of 0.04 rad. before getting it reflected by the curved graphite crystal (002) monochromator of radius 225 mm for high resolution diffraction study. A Xe-gas filled proportional counter (PW1711/90) with electronic pulse height discrimination was mounted on the arm of the goniometer circle of radius 200 mm to receive diffracted X-ray signals. Experimental control and data acquisition were fully automated through computer.

An electronic tensile tester or INSTRON (kmi UTM-201, Capacity, 1000 kgf, load cell, 1000 kgf) was used to study the mechanical properties of both non-irradiated and irradiated PET fibres.

A RAMANOR U 1000, JOBIN YVON, micro Raman set up with a double monochromator designed for high-resolution spectroscopic applications was used for collection of data. The identical monochromators in an additive

**Table 1.** Microstrain by X-ray diffraction.

Sample parameters	I	II	III	IV
Irradiation fluences (n/cm <sup>2</sup> )	0	$1 \times 10^9$	$5 \times 10^{10}$	$1 \times 10^{12}$
Peak position (2 $\mathbf{q}$ , degree)	$23.10 \pm 0.01$	$22.75 \pm 0.01$	$22.62 \pm 0.01$	$22.90 \pm 0.01$
FWHM (2 $\mathbf{q}$ )	12.5	12.5	12.0	12.5
$I_R$ (counts/s)	228	241	307	226
% C	3.4	3.72	4.48	4.78
$d$ (Å)	3.8471	3.9055	3.9277	3.8803
$\mathbf{e}$	0	0.0076	0.0105	0.0043

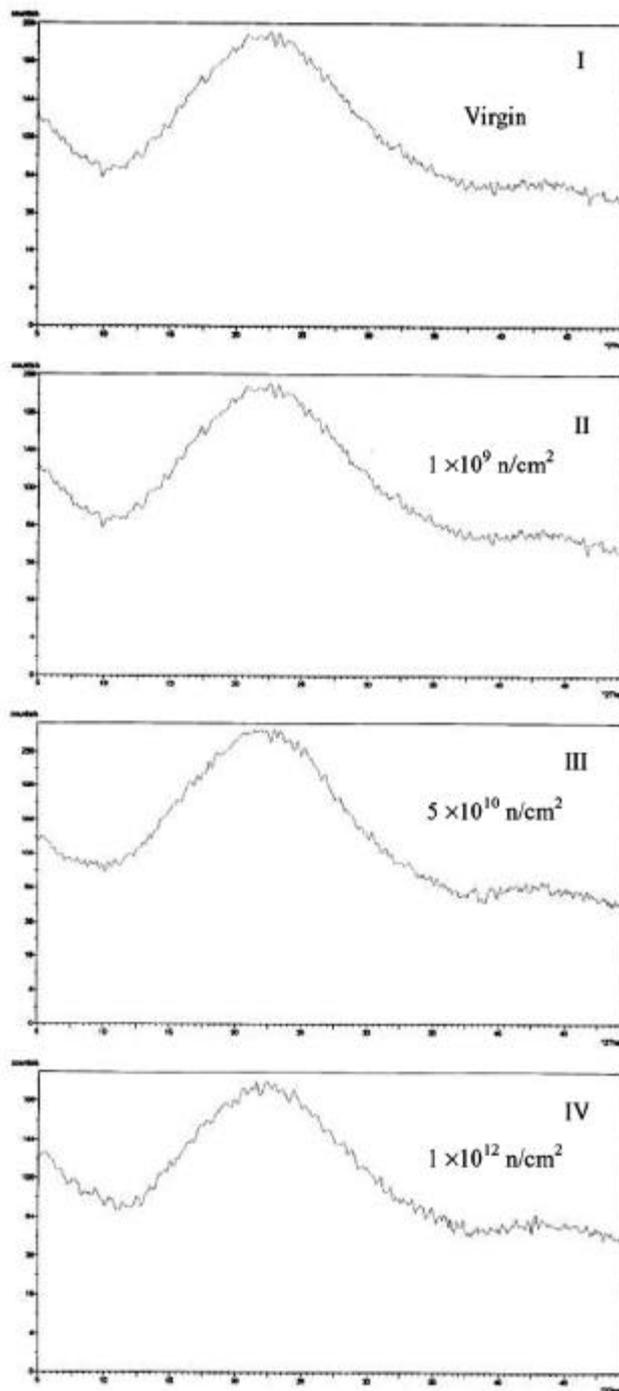
mount equipped with plane holographic gratings having 1800 grooves/mm are used. Each monochromator features an asymmetric Czerny-Turner mounting equipped with 2 slits open symmetrically. The slit width is manually adjustable from 0–3 mm and has been set at 2 mm. The instrument is equipped with 4 collimating mirrors with independent slit and is mounted on Rayleigh type support for fine and reproducible adjustments. The exit slit of the RAMANOR U 1000 is optically coupled with photocathode of the PM tube and interfaced to Spectrum ONE, JOBIN YVON-SPEX, and multichannel detector. The experiments were performed using 514.5 nm green line of an argon ion laser source (3 W). It was focused to give 160 mW of energy and a 20 mm spot on the surface of the fibre. Raman spectra of single fibre were obtained using a Renishaw 1000 Raman microscope at 180° scattering. Spectral data were accumulated at a fixed grating position and collected using a Peltier-cooled CCD camera. The data acquisition is equipped with SPECTRALINK for scanning and recording the wavenumbers and intensity.

The morphology of single PET fibre was investigated using a JEOL JSM-T330 Scanning Electron Microscope (SEM). An electron beam of 5 kV and 0.5 mA was used for the study. The graphite-coated fibre was mounted in cross-sectional mode for investigation.

#### 4. Results and discussion

The diffraction patterns as shown in figure 1 are obtained from the non-irradiated (sample-I) and the irradiated PET fibre (samples II–IV) at different fluences ranging from  $1 \times 10^9$  n/cm<sup>2</sup>– $1 \times 10^{12}$  n/cm<sup>2</sup>. PET is semi-crystalline in nature. The XRD pattern of virgin PET fibre obtained shows that it is mostly amorphous in nature with less amount of crystallinity. The tip of the amorphous halo of the virgin has been observed at  $2\theta = 23.1^\circ$  in the diffraction pattern as shown in the diffractogram (figure 1 (I)). Only small changes were obtained in the XRD pattern of the irradiated PET samples as compared to the virgin one. Amorphous peak tips of all other irradiated samples were found to be shifted slightly towards lower angle, the results of which are presented in table 1. The change in relative intensity ( $I_R$ ) and the shift in angular position can be explained by a change in lattice spacing (Guzman *et al* 1985). If the crystal is given a uniform tensile strain at right angles to the reflecting planes, their  $d$  spacing becomes larger than original, and the corresponding diffraction line shifts to lower angle (Cullity 1978). So the shifting of the diffraction peak position in the diffractogram of the samples towards lower angle is because of the microstrain developed in the PET crystallites due to neutron irradiation. This microstrain developed due to irradiation was calculated using (5) and has been tabulated in table 1. Microstrain of the PET fibre under investigation shows a peculiar value, which initially increases up to certain fluence and then decreases with radiation

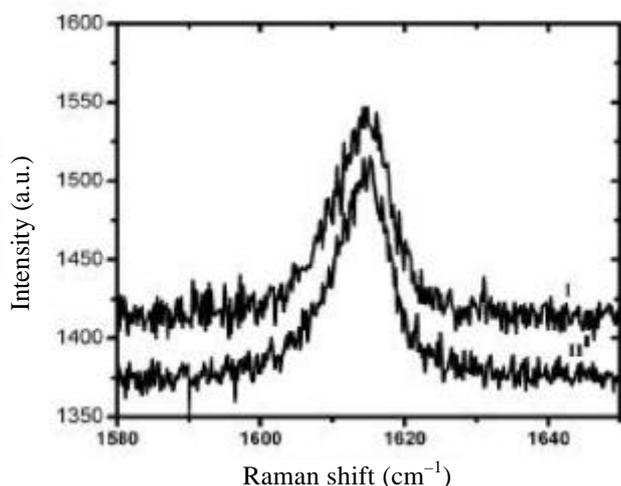
dose. The angular shift can be explained on the basis of the Hosemann's (1967) paracrystals theory, where semicrystalline polymers possess two types of disorders as compared to an ideal well-ordered crystalline structured cell. In a crystalline cell long-range ordering shows statistical fluctuations resulting in a decrease of X-ray diffraction peaks intensity. On the other hand, second type disorders



**Figure 1.** X-ray diffraction pattern of PET fibre sample before (I) and after (II, III and IV) irradiation with 4.44 MeV neutron at different fluences.

**Table 2.** Mechanical properties by INSTRON.

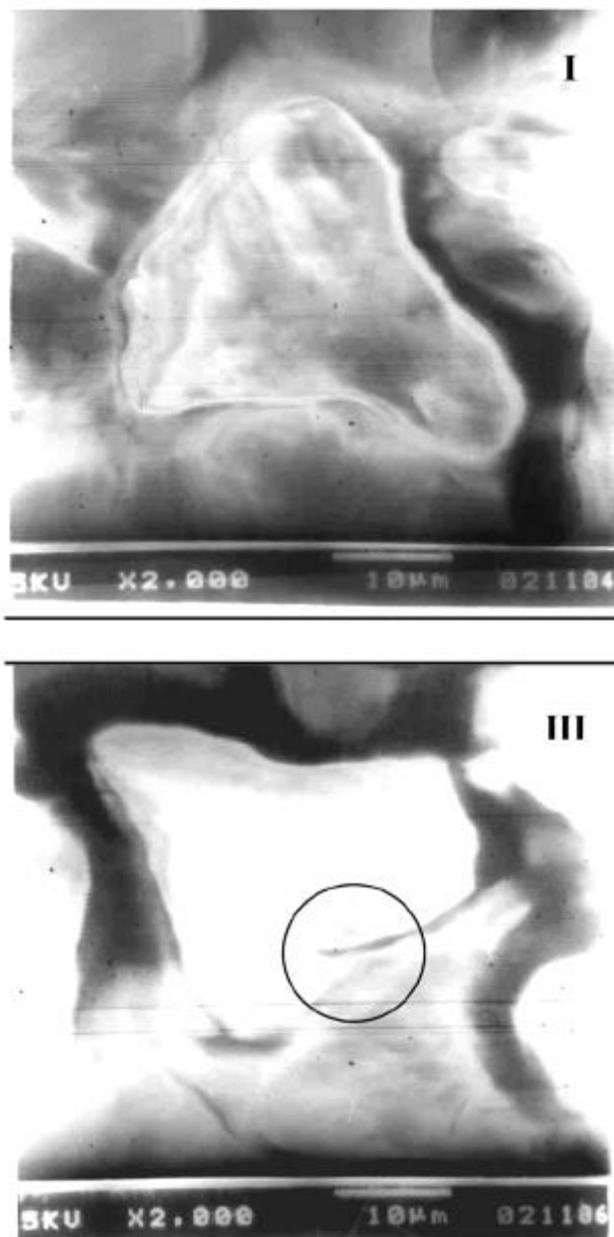
Sample parameters	I	II	III	IV
Ultimate tensile strength (kg/mm <sup>2</sup> )	0.345	0.660	0.487	1.036
Young's modulus (GPa)	4.508	5.211	3.816	6.766



**Figure 2.** Variation of wavenumber and intensity of peak position of 1614.70 cm<sup>-1</sup> Raman band from a single filament PET yarn of virgin (I) or unstrained and neutron irradiated (fluence  $5 \times 10^{10}$  n/cm<sup>2</sup>) samples (III).ly

correspond to small fluctuations in the separation distance between monomeric units, which result in both a decrease in intensity and a broadening of diffraction peak (Crist and Cohen 1979; Martinez-Pardo *et al* 1998). Since the fibre sample taken for the present study does not have an ideal and well-ordered crystalline structure, the intensity shows a reverse effect (increases) with the exception of sample-IV. The FWHM of amorphous halo so obtained are very broad indicating the existence of either poorly formed crystallites or very small crystalline domains, which are insufficient in size to cause good X-ray diffraction (Alexander 1969). Such broad spectra make determination of crystallinity very difficult, as it is not possible to determine accurately the amorphous halo. The predicted amorphous background for subtraction is generated by pro-fit software (Philips Analytical X-ray, Netherlands, 1999). Crystallite dimension of the virgin sample was found to be around 7.14 Å, which increases slightly due to neutron irradiation and is reported in a separate paper (Mallick *et al* 2004).

Measurement of tensile properties of fibre is very important to understand the mechanical behaviour of the fibre in actual practice. The experimental results obtained are presented in table 2. It is observed that the ultimate tensile strength (kg/mm<sup>2</sup>) of the PET fibre increases with radiation dose. But the sudden decrease in tensile strength value (0.487) of sample III is because of large micro-



**Figure 3.** SEM micrographs of virgin (I) and neutron irradiated (III) PET fibres.

strain developed due to neutron irradiation at fluence  $5 \times 10^{10}$  n/cm<sup>2</sup>. The Young's modulus shows an improvement in the PET fibre due to irradiation, with an exception at sample III. From the above result, we found that, at the fluence of  $5 \times 10^{10}$  n/cm<sup>2</sup> the fibre sample possesses

less Young's modulus as compared to the fluences of  $1 \times 10^9$  n/cm<sup>2</sup> because of highest value of microstrain developed in the crystallites.

The Raman band observed (figure 2) from virgin (I) fibre sample at  $1614.65 \text{ cm}^{-1}$  is related to a vibration with C=C stretching because of strong aromatic character. The Raman shift increases to  $1615.10 \text{ cm}^{-1}$  for sample III irradiated at a fluence of  $5 \times 10^{10}$  n/cm<sup>2</sup>, though the change in position of Raman band in PET fibre is stress dependent (Young and Yeh 1994). So increase in wavenumber and decrease in intensity of Raman shift is probably due to strain developed because of high-energy radiation heating. The above micro-Raman spectral data also support the XRD results related to strain.

Again at a particular fluence the polymer gets cross-linked. The cross-linked polymer possesses improved mechanical properties. Before the cross-linking point the polymers degradation and breaking (fracture) of polymer molecules started due to irradiation. The point where the breaking is maximum, the fibre possesses low tensile strength as compared to the cross-linked fibre. The fracture observed in the single PET filament as in SEM micrographs (figure 3) supports the above XRD, INSTRON and micro-Raman results. Hence we may conclude that in a continuous neutron irradiation the PET fibre attains a new state of modification just before the cross-linking point where breaking (fracture) is high with large strain value. In the present analysis the fluence required to attain the above new state in PET fibre is about  $5 \times 10^{10}$  n/cm<sup>2</sup>.

## 5. Conclusions

The crystallinity of the fibre obtained by X-ray diffraction shows that the % crystallinity increases with neutron fluences, which indicates enhancement of its mechanical strength. But the experimental measurement of ultimate tensile strength (kg/mm<sup>2</sup>) and Young's modulus by INSTRON does not satisfy with the above prediction of the mechanical properties for the sample irradiation at fluence,  $5 \times 10^{10}$  n/cm<sup>2</sup>. The failure of the mechanical property is because of the microstress developed in the grains of the PET fibre due to neutron irradiation. The microstress developed due to neutron irradiation was calculated using microstrain value ( $\epsilon$ ) from X-ray diffraction results and the initial Young's modulus ( $E$ ) from INSTRON results. Microstress values of the irradiated samples II, III and IV were found to be 0.0396, 0.0401 and 0.0291 GPa, respectively. The highest value (0.0401 GPa) of microstress in case of sample III causes mechanical failure of fibre material easily.

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