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Section – PHYSICAL SCIENCES

STRUCTURAL INVESTIGATION OF NORMAL AND TREATED POLYESTER FIBERS BY SAXS AND OTHER TECHNIQUES

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ABSTRACT

Macromolecular parameters of normal and treated (acid & alkali) polyester fiber have been investigated using Small Angle X-ray Scattering (SAXS) technique. The theories of Vonk[1] and Ruland [2] have been applied treating the fiber as non-ideal two-phase system. Intensity data was collected using compact Kratky camera. Three and one-dimensional correlation functions were computed from background corrected SAXS profiles and parameters like width of transition layer (E), average periodicity transverse to layer (D), specific inner surface (S/V), length of coherence (l_c), transversal lengths in matter and void ($\bar{l}_1 \& \bar{l}_2$), range of inhomogenity (l_r), volume fractions of matter and void (ϕ_1 & ϕ_2), volume fraction of transition layer ($2E_v/D$) and characteristic number (f_c) were determined. Furthermore, parameters were obtained from SEM, INSTRON and XRD. The simulation results related to

above parameters confirm that strong acid & strong alkali affect the fiber to some extent at ambient temperature.

INTRODUCTION

The sample used for investigation in the present work is Polyester, a synthetic fiber which has build its importance in the textile industries and also in the field of microelectronics and solid state devices because of its strength, inertness and thermal stability [3]. SAXS study on normal and treated polyester fibers facilitates determining various micro and macromolecular parameters and hence shows the effects of acid & alkali on polyester fiber.

The work of Patel et al [4] on Nylon 6 shows that synthetic polymers possess non-ideal two-phase structure. The analysis of scattering data of polyester reveals that it belongs to non-ideal two-phase system.

Polymers often exhibit deviation from Porod [5,6] law. The product $\widetilde{I}p(s)\cdot s^3$ does not lead to a constant value at large $s(=2\cdot\sin\theta/\lambda)$ but leads to either positive or negative deviation. Negative deviation[7,8] has been observed in semi-crystalline polyester due to crystal surface irregularities and the existence of diffuse phase boundary causing depletion of intensity at high angles.

Ruland [2] has modified Porod's law to determine density fluctuation and width of transition layer. Vonk [1] has developed practical aspects of Ruland method, which have been followed in this work.

SAMPLE

The polyester fiber used for our investigations was obtained from a private firm. The details can be obtained from work done by Bal et al.[9].

Chemicals such as strong acids and alkalis are used in many cleaners and batteries. The effect of these reagents may have on the fibers in the chemical processes during preparation, dyeing, printing and finishing treatments. Compounds that destroy, dissolve or weaken a fiber cannot be used in these processes. Polyester fibers interact with detergents, soaps etc. while in use. Moreover these fibers are also subjected to dry cleaning. Therefore it is important to understand the effects of alkalis and acids on these fibers. In this paper an attempt to investigate the effects of above on polyester fiber has been done.

EXPERIMENTAL

A part of the sample was soaked in Sulphuric acid solution at concentration pH 1 and another part of the sample was soaked in Sodium Hydroxide solution at concentration pH 12. The samples are kept in these conditions for 48 hours at ambient temperature and then they were washed with distilled water and dried.

SAXS intensity data for untreated (here called sample-0) and treated sample with H_2SO_4 of pH 1 (called sample-I) & with NaOH of pH 12 (called sample-II) were collected using compact Kratky camera having counter attachment. A Phillips PW 1729 X-ray generator with a copper target operated at 35 kV and 20 mA[10] was used for collection of intensity data. The entrance and counter slit attached to the Kratky camera were adjusted at 80 μm and 250 μm respectively. The room temperature was maintained at 22.5 ± 0.5 ^{0} C and sample to counter distance was 20 cm. Monochromatic Cu k_α (λ=1.54 A^0) radiation was obtained using a nickel filter of 10 μm thickness which was used to irradiate polyester fibers packed in Mark capillary tube of 1 mm diameter. The intensity data have been collected keeping the sample both in parallel and perpendicular positions to the X-ray beam for testing its isotropic nature. To avoid parasitic scattering by air present between sample and detector the irradiation was carried out under a vacuum of approximately $\frac{1}{2}m\,\text{bar}$[11]. The smeared out intensity curve (Fig.1) was plotted by subtracting blank capillary data from observed scattering data. Constant background intensity has been subtracted from observed data according to Konrad and Zachmann[12] for the purpose of estimation of different parameters of the samples.

Mechanical parameters like Young's modulus and percentage elongation of the samples were found out using INSTRON equipment. Furthermore, diameters are obtained from SEM photographs and crystallinity measurements were done from XRD study.

THEORY

Theories of Vonk[1] and Ruland[2] have been applied here to calculate various macromolecular parameters, treating the sample as a non-ideal two-phase system having isotropic structure. An important parameter in characterization of structure is given by

$$R = \frac{\left\langle \left| grad\eta \right|^2 \right\rangle}{\left\langle \eta^2 \right\rangle} = 4\pi^2 \frac{\int_0^\infty s^4 I(s)ds}{\int_0^\infty s^2 I(s)ds} = 6\pi^2 \frac{\int_0^\infty s^3 \tilde{I}(s)ds}{\int_0^\infty s\,\tilde{I}(s)ds} \quad \text{..................................(1)}$$

where *I(s)* and $\tilde{I}$ *(s)* are desmeared and smeared out intensities respectively in arbitrary units , η is deviation of electron density from its mean value, *s* is a vector in a reciprocal (Fourier) space. In an ideal two-phase system, the gradient at phase boundary is infinity and *R* also goes to infinity. The case where the minimum value of $R = 4\pi^2 s_0^2$ corresponds to the intensity function *I(s)* consisting of a single peak at $s = s_0$. Such an intensity function is obtained from a randomized layer structure. Here electron density perpendicular to layers fluctuates according to a sine function.

Further R has been expressed in terms of intensity function *I(x)* by T. Patel et al. [13,14] as

$$R = 3/2\,(2\pi/\lambda\, a)^2 \int_0^\infty x^3 \tilde{I}(x)dx \Big/ \int_0^\infty x\tilde{I}(x)dx \quad \text{.......................................(2)}$$

where x is the position co-ordinate of the scattered intensity from the centre of primary beam , a, distance of sample from the counter slit and $s = 2\theta/\lambda = x/\lambda a$, 2θ is the scattering angle. Small, positive and finite value of *R* suggests that corrugation at the phase boundary exists and electron density changes from matter phase to void phase over a transition layer E and in consequence Porod's law, fails.

The width of transition layer *E* can be obtained from the relation derived by Vonk[1]

$$E = (-4/R)(dC(r)/dr)_{r=E_V} \quad \text{................ ....(3)}$$

where *C(r)* is the three-dimensional correlation function of a sample normalized to unity at the origin in real space. The function *C(r)* was derived by Mering and Tchoubar[15] and expressed in terms of 'x' by T. Patel et al. [14] as

$$C(r) = \int_0^\infty x\tilde{I}(x)J_0(2\pi r x/\lambda\, a)dx \Big/ \int_0^\infty x\tilde{I}(x)dx \quad \text{........... ....(4)}$$

J_0 is Bessel function of zero order of the first kind. According to Vonk[1] for an isotropic sample

$$R = -3\left(d^2C(r)/dr^2\right)_{r=0} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

However whenever R is determined from the correlation function care must be taken to avoid experimental error at the tail of the scattering curve as the correlation function in the origin is very sensitive to such error as pointed out by Caulfield and Ullman [16].

One- dimensional correlation function $C_1\ (y)$ given by Kortleve and Vonk[17] for layer structure in terms of x[14] is expressed as

$$C_1(y) = \int_0^\infty x\tilde{I}(x)[J_0(z) - zJ_1(z)]dx \Big/ \int_0^\infty x\tilde{I}(x)dx \ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where $z = 2\pi xy/\lambda a$ and J_1 is the Bessel function of first order and of the first kind. According to Vonk[1] the position of first subsidiary maximum in the one-dimensional correlation function $C_1(y)$, gives the value of the average periodicity D transverse to the layers.

The specific inner surface defined as the phase boundary per unit volume of
the dispersed phase is.

$$(S/V)=2/D \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

The relation

$$\langle\eta^2\rangle/\langle\Delta\eta\rangle^2 = \varphi_1\varphi_2 - (ES/6V) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

was given by Vonk where $\phi_1,\ \phi_2$ are the volume fraction of matter and void region respectively and the relation $\phi_1 + \phi_2=1$ can be used to determine the individual values of ϕ_1 and ϕ_2.

As defined by Mittelbach and Porod[18] for a two-phase system transversal lengths of matter and void phases for a three-dimensional system are given by the relation

$$\bar{l}_1 = 4\phi_1(V/S), \quad \bar{l}_2 = 4\varphi_2(V/S) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

and $$1/\bar{l}_r = 1/\bar{l}_1 + 1/\bar{l}_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

where $\bar{l}_r$ is the range of inhomogenity. Moreover,

$$l_c = 2\int_0^\infty C(r)dr \text{ ……………………. ……………………. ……………. } (11)$$

l_c being the length of coherence which is the average value of length of cords drawn in all directions. A second method to determine the width of transition layer E as given by Ruland[2] for a non-ideal two phase system and expressed in terms of x is given by

$$\tilde{I}(x) \cdot x = \pi C/\ 2 \cdot (\lambda a)^3 \cdot x^{-2} - \pi^3 C/3 \cdot (\lambda a) \cdot E^2 \text{ ………………….. } (12)$$

From the above equation the plot of $\tilde{I}$ *(x)* . *x* versus x^{-2} at the tail end of the SAXS pattern is known as Ruland plot. Equation 12 reduces to Porod's law if $E=0$, for an ideal two-phase system.

RESULTS AND DISCUSSION

Five intensity values $\tilde{I}(x)$ near the origin were fitted to a Gussian curve *(x).*

$$\tilde{I}(x \to 0) = p \cdot \exp(-qx^2)$$

by least square technique. The values of p for sample 0, I and II were obtained as 73339, 79369 and 83004 $Jm^{-2}\ s^{-1}$ respectively and corresponding values of q as 97.29, 95.8 and 97.55 m^{-2} respectively. The scattering curves were extrapolated to zero angle by using values of p and q (Fig-1) indicating the extrapolated points by symbol Δ. The method of extrapolation has very little effect on the relevant part of the correlation functions i.e. position and height of first subsidiary maximum of the one-dimensional correlation function is not affected much [14]. Values of R were determined using equation (2) and were found to be (23.12 ± 0.28) $10^{-4}\, A^{0^{-2}}$, (26.58 ± 0.31) $10^{-4}\, A^{0^{-2}}$ and (26.36 ± 0.31) $10^{-4}\, A^{0^{-2}}$ for sample-0, sample-I and sample-II respectively. Small and positive values of R parameter for all samples prove that electron density gradient at phase boundary is finite thus suggesting belongingness of sample to a non-ideal two-phase system. Values of R obtained by relation (5) using five-point forward difference method were found out to be (23.12 ± 0.03) $10^{-4}\, A^{0^{-2}}$, (26.25 ± 0.03) 10^{-4} $A^{0^{-2}}$, and (26.12 ± 0.08) $10^{-4}\, A^{0^{-2}}$ for sample-0, sample-I and sample-II respectively. These figures are almost equal to the values of R of the corresponding samples that were already obtained using equation (2), which indicates isotropic nature of the sample. The symmetric intensity pattern in Fig. 2 also indicates the isotropic nature of the sample. The difference of intensity corresponding to the two types of mounting of sample is due to the difference in quantity of sample exposed [9,19,20].

For various values of r and y, the three- and one-dimensional correlation function for the samples were computed respectively and are shown in Fig.3 and Fig. 4 with error bars. According to Vonk the width of transition layer (*E*) was obtained from the plot of $\left(-\frac{4}{R}\right)\cdot\left[\frac{dC(r)}{dr}\right]$ versus r in fig. 5.

The value of average periodicity transverse to the layers (*D*) were obtained from the position of first subsidiary maximum in one-dimensional correlation function (Fig. 4). The value of the specific inner surface (S/V), the volume fractions of matter and void (ϕ_1 and ϕ_2), the transversal lengths in matter and void ($\bar{l}_1 \& \bar{l}_2$), range of inhomogenity (l_r), the length of coherence (*lc*) were estimated. All main SAXS parameters are tabulated in Table-1.

Ruland Plot $\widetilde{I}(x)$ x versus x^{-2} of the two samples are shown in Fig.6 which give straight lines at the limiting region of the scattering curve where slopes are (98±0.04), (104.04±0.28) , (138.72±0.1) and y intercepts are (-248.99 ± 1), (-231.30 ± 1.3), (-322.16 ±0.5) of samples 0, I and II respectively. Using these slopes and intercepts, the width of transition layer (E_R) by Ruland method were found out which is quite close to E_v(Table-1). Standard deviation of the intensities $\sigma(I)^{1/2}$ was calculated at tail region of SAXS curve of samples and values are well within the permissible limits[21] (0.5) (Table-1). The regression coefficient γ for sample-0 = 0.91, sample-I = 0.95 and for sample-II = 0.9 confirms the accuracy of collected data[22]. Lamellar models for the three samples are shown in Fig. 7, which are based on findings of SAXS parameters (table-1).

The average diameters of the three sample fibers obtained from SEM study are 2150×10^2 A^0, 1900×10^2 A^0 and 2000×10^2 A^0 respectively. The SEM micrographs of samples at different magnifications are shown in Fig. 8. Each SEM photograph contains a dark and bright region clearly indicating the two-phase nature of the sample. Moreover the photographs at 5000 magnification clearly show that there is no preferred orientation of the matter in any direction confirming isotropic nature of the sample.

Tensile study shows that percentage elongation of sample-0, sample-I and sample-II are 20 %, 33.7% & 28 % and Young's moduli of the same are 3.9×10^9 N/m^2, 2.3×10^9 N/m^2 & 2.8×10^9 N/m^2 respectively.

Parameters of respective samples estimated from the corresponding X-ray Diffractograms (shown in Fig. 9) are presented in Table-2 .

CONCLUSIONS

The values of $C(r)$ show damped oscillatory behavior at large values of r [17, 23] for non-ideal two-phase system and this trend is evident for all the samples. Negative intercepts of Ruland plot confirm the non-ideal two-phase nature. The values of width of transition layer E_v and E_R obtained by the methods of Vonk (E_v) and Ruland (E_R) are nearly equal confirming the correctness of collected data and method of analysis. The slight increase in the value of specific inner surface (S/V) and decrease in the value of D of sample-I & sample-II as compared to the corresponding parameters of original sample (Table-1) shows that acid & alkali treatment has some effect on the sample. The value of ϕ_1 and l_1 of the treated samples decrease and that of ϕ_2 and l_2 increase as compared to corresponding parameters of untreated sample (Table-1) indicating that the fiber undergoes degradation thereby decreasing the width of the matter phase (Fig. 7).

The values of the diameters of samples obtained from SEM study show that there is slight reduction in the diameter of the fiber when treated with strong acid & alkali. Increase in percentage elongation and decrease in Young's modulus of the fiber in treated samples (sample-I & II) concludes that macromolecules of the fiber degrade.

Wide angle X-ray scattering shows that there is decrease in crystallite size (t) as evident from the increase in the half width of peaks (Δw) in treated samples in comparison to sample-0 (table-2). In addition, there is decrease in the percentage crystallinity (C) and in the Bragg spacing (d) in the above treated cases. This may be due to considerable destruction of crystallites.

The findings obtained from SAXS are consistent with the results obtained through SEM, XRD and INSTRON studies. These conclusions confirm that polyester fiber is affected by some extent when treated with acid and alkali of higher concentration (pH). In essence the fiber degrades more in strong acid compared to strong alkali that is evident from above comparison of parameters. However precautionary measures need to be taken while using strong acids and alkalis particularly at higher temperatures.

REFERENCES:

[1] C. G Vonk , *J. Appl. Crystallogr.* , **6**, 81(1973).

[2] W. Ruland, *J. Appl. Crystallogr.* **4**, 70(1971).

[3] N. V. Bhat and S. G. Naik, *Textile Research Journal*, **54,** 868(1984).

[4] T. Mishra, S. S. Khuntia, V. H. Buch and T. Patel, *Polym . J.*, **24**, 323(1992).

[5] G.Porod , Kolloid Z. ,**124 ,**83(1951).

[6] G.Porod , Kolloid Z. ,**125 ,**51(1952).

[7] E. Helfand, *Acc. Chem. Res.*, **8**, 295(1975)

[8] E .Helfand and Y. Tagami *Polym. Lett***. 9,** 741 (1971).

[9] T.Patel and S.Bal, *Polym . J.*, **33(2)**, 121(2001).

[10] O. Glatter and O. Kratky, “Small Angle X-Ray Scattering,” Academic Press, New-York, N. Y., 1982, p-435.

[11] R. W. Hendricks, *J. Appl. Crystallogr*, **3**, 348(1970)

[12] G .Konrad and N. G Zachmann, *Kolloid Z. Z. Polym***. 247 ,** 851(1971)

[13] T. Mishra, D. K. Bisoi, T. Patel, K. C. Patra and A. Patel, *Polym . J.*, **20**, 739(1988).

[14] T. Mishra, K. C. Patra and T. Patel et. al, *Colloid.Polym. Sci.,* **262,** 611(1984).

[15] J. Mering and D. Tchoubar, *J. Appl. Crystallogr*. **1** 153(1968)

[16] D. Caulfield and R. Ullman, *J. Appl. Phys*, **33**,1737(1962).

[17] G. Kortleve and C G Vonk *Kolloid Z. Z. Polym.* **225,** 124(1968).

[18] P. Mittelbach and G. Porod *Kolloid Z. Z.* Polym. **202** 40(1965).

[19] T. Mishra, P. Panda, T. Patel, D. K. Bisoi and D. K. Panda, *Jpn. J. Appl-Phys*, **32**, 4615(1993).

[20] T. Mishra, J. Shukla, MD. N. Khan, D. K. Bisoyi and T. Patel, *Polym . J.*, **29**,1007(1997).

[21] C. G Vonk , *J. Appl. Crystallogr.* , **4**, 340(1971).

[22] J. Topping "Errors of Observation and their treatment:"4th Edition ,Chapman and Hall London, (1972), p-82 and p-104

[23] T. Patel and S. Bal, *Bulletin of Orissa Physical Society*, **VIII**, 74(2000)

TABLE-1

PARAMETERS	SAMPLE-0	SAMPLE-I	SAMPLE-II
D(A^0)	319	296	301
E_v (A^0)	21.2 ± 0.017	19.2± 0.017	19.2 ± 0.017
E_R (A^0)	19.13 ± 0.04	17.91± 0.05	18.3 ± 0.016
S/V (A$^{0-1}$)	0.0063	0.0067	0.0066
ϕ_1	0.846± 0.004	0.825± 0.004	0.83 ±0.004
ϕ_2	0.154 ± 0.004	0.175± 0.004	0.17 ± 0.004
$2E_V/D$ (%)	13.29 ± 0.01	12.97± 0.01	12.76 ± 0.01
l_1(A^0)	540 ± 2.55	488.40± 2.37	499.66 ± 2.41
l_2(A^0)	97.99 ± 2.55	103.60± 2.37	102.34 ± 2.41
I_r(A^0)	82.94 ± 0.011	81.69± 0.011	81.63 ± 0.011
I_c(A^0)	127.71 ± 0.22	123.86± 0.21	125.49 ± 0.21
σ	0.16	0.23	0.19
γ	0.91	0.95	0.9

TABLE-2

Sample	Peak No	2θ (degrees)	Half Peak Width ($\Delta w = \frac{\phi_2 - \phi_1}{2}$) (degrees)	Bragg Spacing ($d = \frac{n\lambda}{2\sin\theta}$) ($\overset{0}{A}$)	Crystallite Size ($t = \frac{0.9\lambda}{\Delta w \cos\theta}$) ($\overset{0}{A}$)	Percentage Crystallinity (C in %)
Polyester-0	1	17.4	1.45	5.09	55.48	25
	2	23.5	2.75	3.79	29.53	
	3	26.1	2.15	3.41	37.96	
Polyester-1	1	17.7	1.75	5.01	45.98	

	2	23.5	2.95	3.79	27.53	19.85
	3	25.5	2.45	3.49	33.27	
Polyester-12	1	18.0	1.80	4.93	44.73	20.23
	2	23.3	2.90	3.82	27.99	
	3	25.6	2.45	3.48	33.28	

FIGURE CAPTIONS

Fig. 1 *Smeared out scattering curve of sample-0, I and II are shown in (A), (B) and (C) respectively. Extrapolated points are shown by* Δ *sign.*

Fig. 2-*Smeared out Scattering curves (Horizontal and vertical mounting) Extrapolated points are shown by* Δ *sign.*

Fig. 3 *Three Dimensional Correlation Function ' C(r)' against 'r' with error bars of of sample-0, I and II*

Fig. 4 *Curves of one dimensional Correlation Function '*C_1 *(y)' against 'y' with error bars* of *of sample-0, I and II*

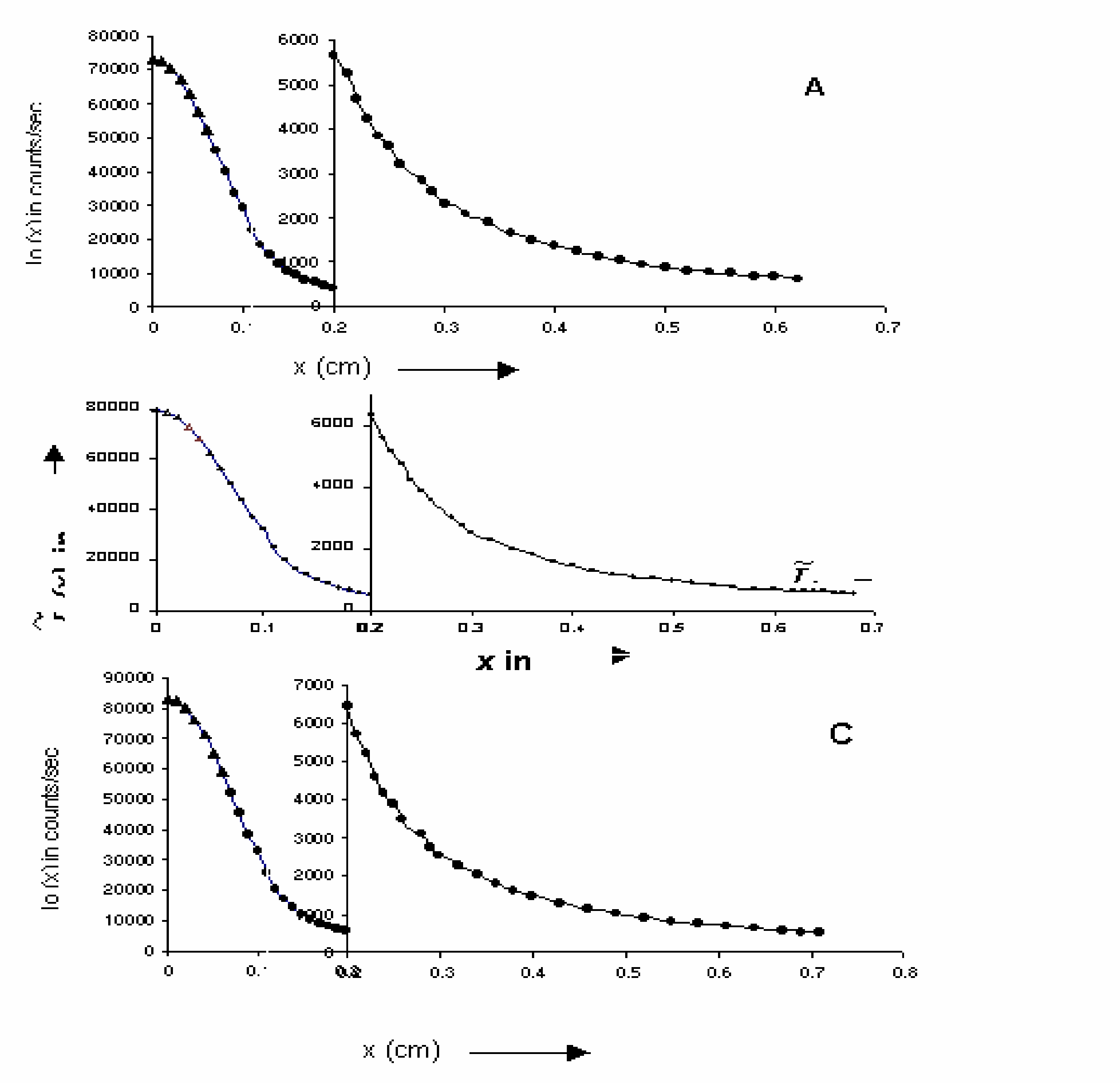
Fig. 5 *Curves of '-4R (dC(r)/dr)' against 'r' of sample-0, I and II*

Fig. 6 *Ruland Plot of I(x)x against* x^2 *of sample-0, I and II*

Fig. 7 *Lamellar model drawn to the scale (***100 A^0= 1 cm***) of Sample-0(Fig.A), Sample-I(Fig. B) and Sample-II(Fig. C);* **M***, matter;* **V***, void ;* **D***, periodicity transverse to layer;* **E***, width of the transition layer;* d_1&d_2*, number averages of the thickness in matter and void regions respectively.*

Fig. 8 *SEM micrographs of SAMPLE-0 (shown in 1(a), 1(b) and 1(c)), SAMPLE-I (shown in 2(a), 2(b) and 2(c)) and SAMPLE-II (shown in 3(a), 3(b) and 3(c)) at different magnifications.*

Fig. *9 X-ray diffractogram of SAMPLE-0 , I and II denoted as polyester 0, 1 and 12 respectively.*



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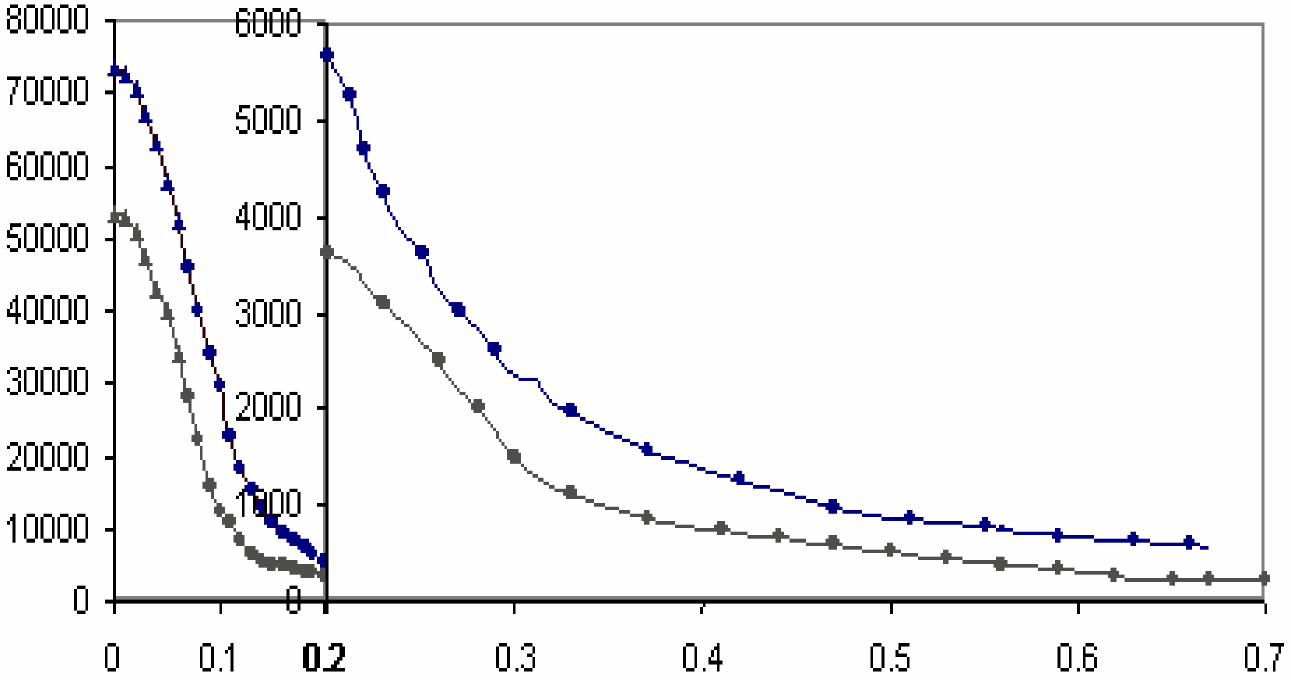


Fig. 2-*Smeared out Scattering curves (Horizontal and vertical mounting) Extrapolated points*

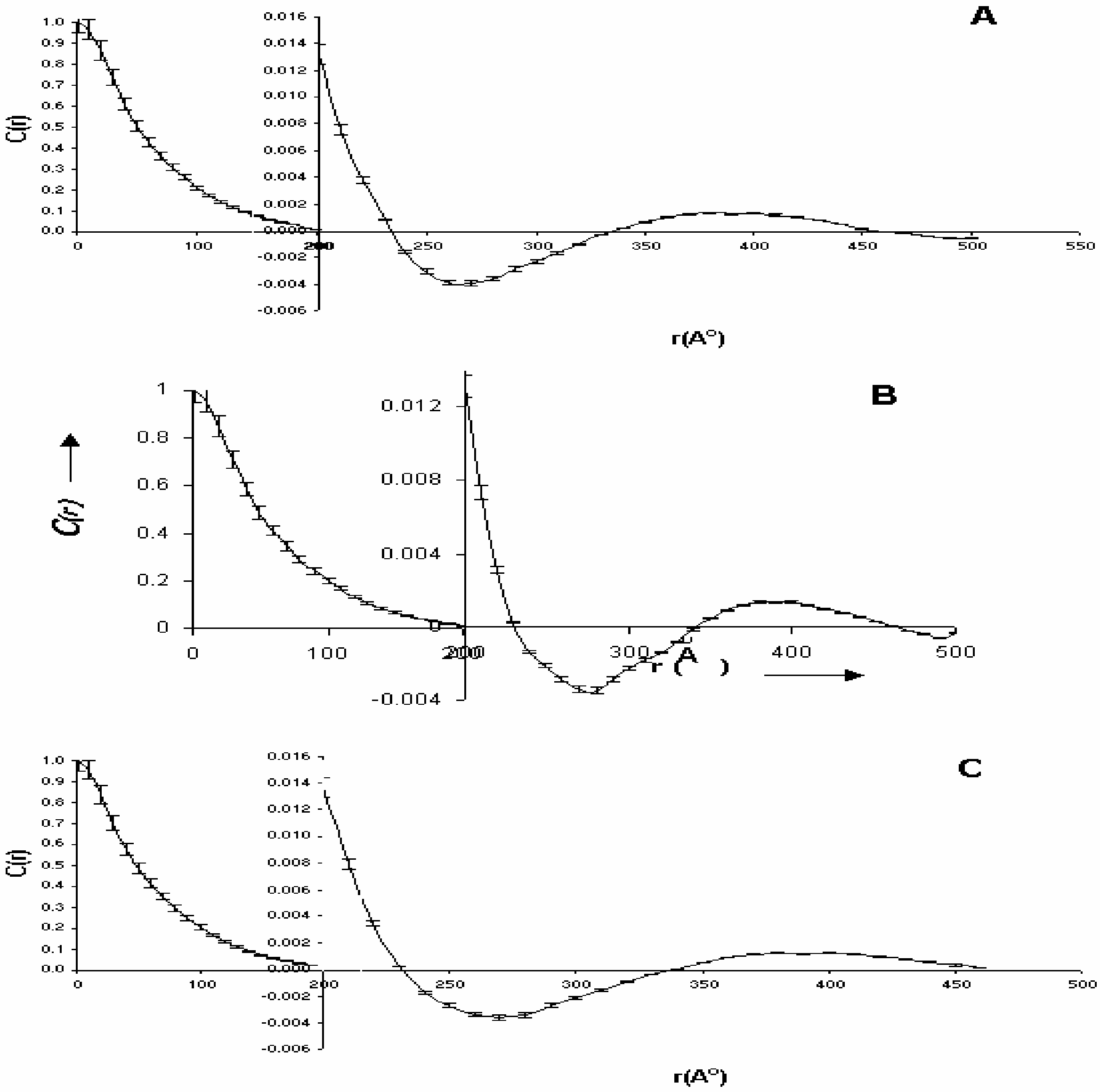


Fig. 3 *Three Dimensional Correlation Function ' C(r)' against 'r' with error bars of of sample-0, I and II*

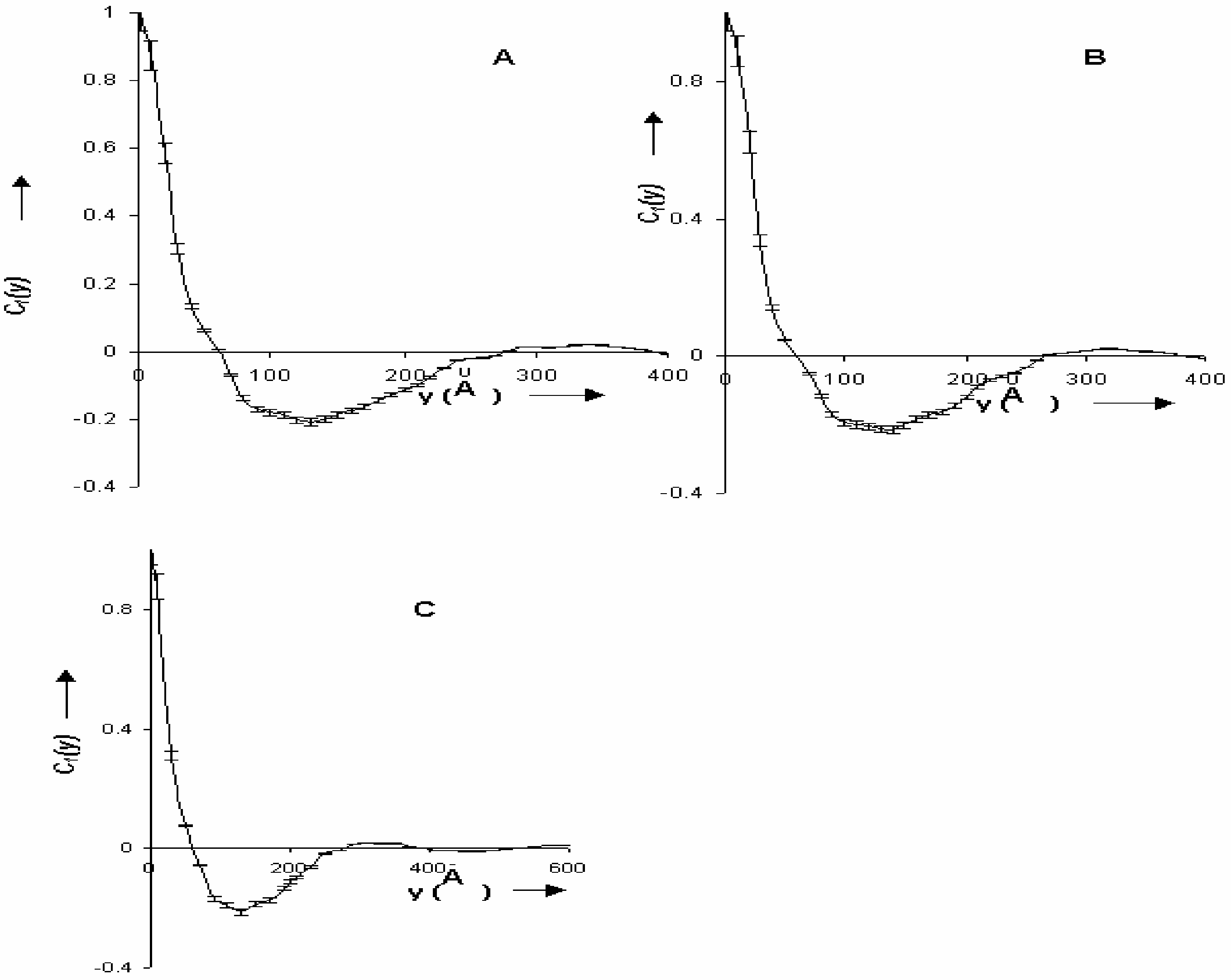


Fig. 4 *Curves of one dimensional Correlation Function 'C_1 (y)' against 'y' with error bars* of *of sample-0, I and II*

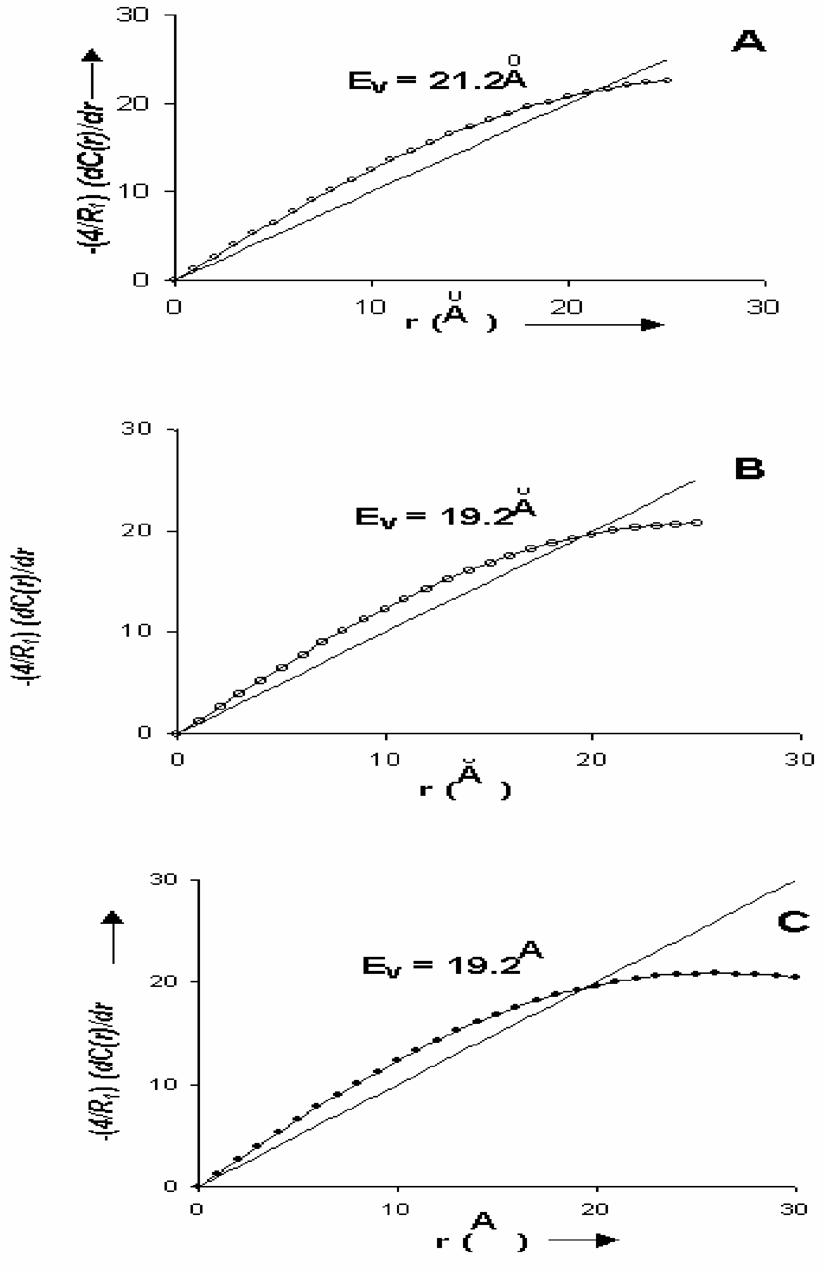


Fig. 5 Curves of '-4R (dC(r)/dr)' against 'r' of sample-0, I and II

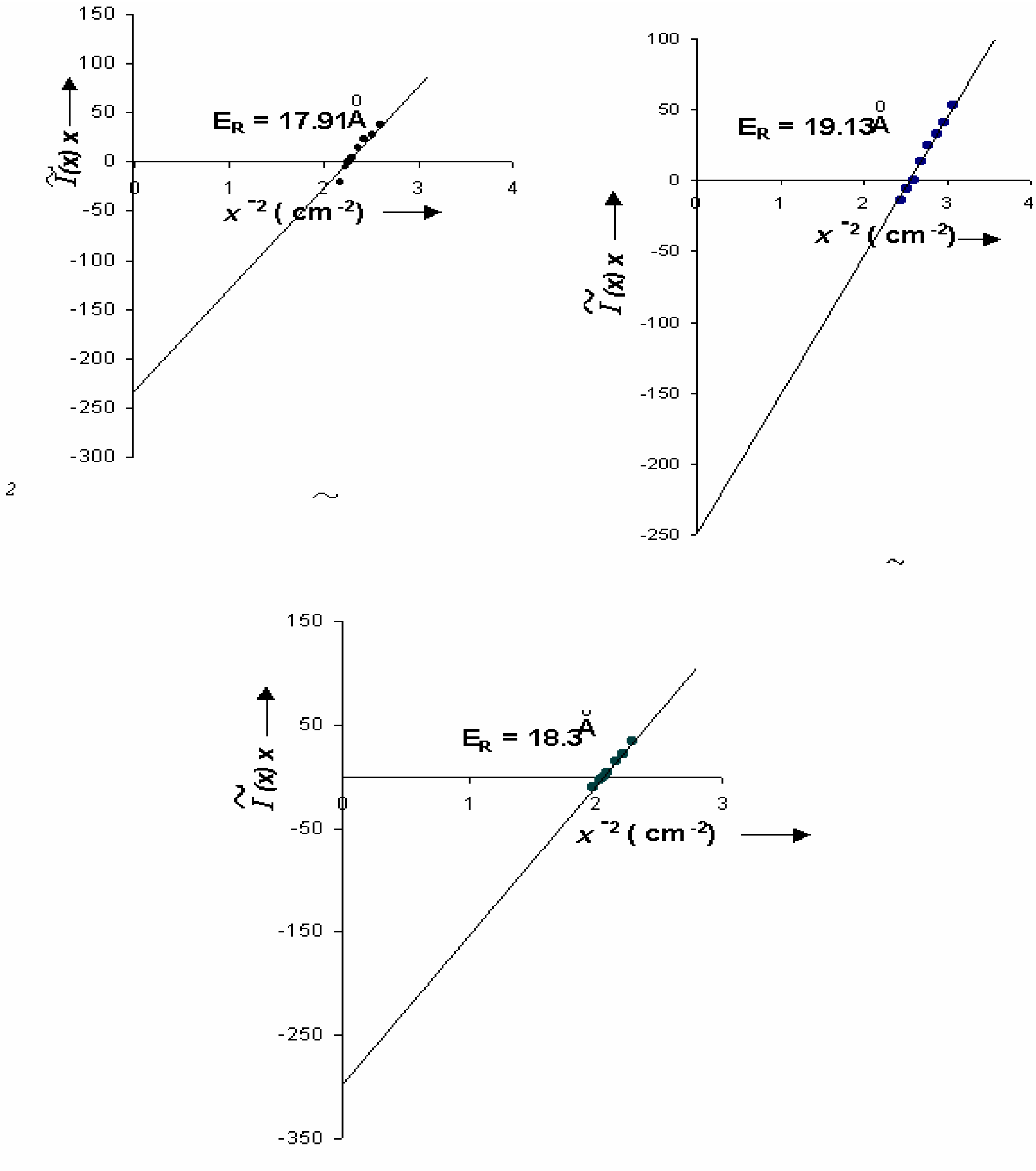
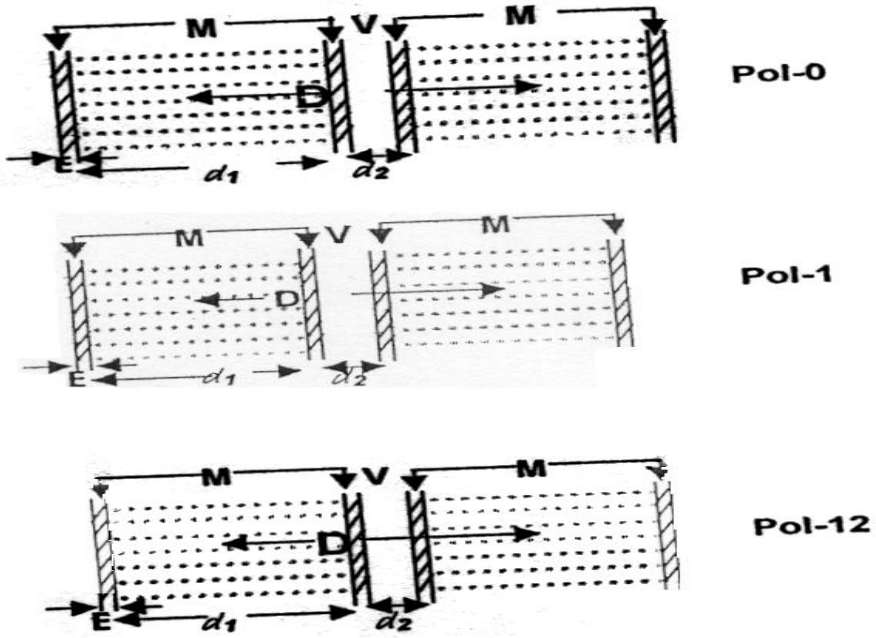


Fig. 6 *Ruland Plot of* $\widetilde{I}(x)x$ *against* x^2 *of sample-0, I and II*



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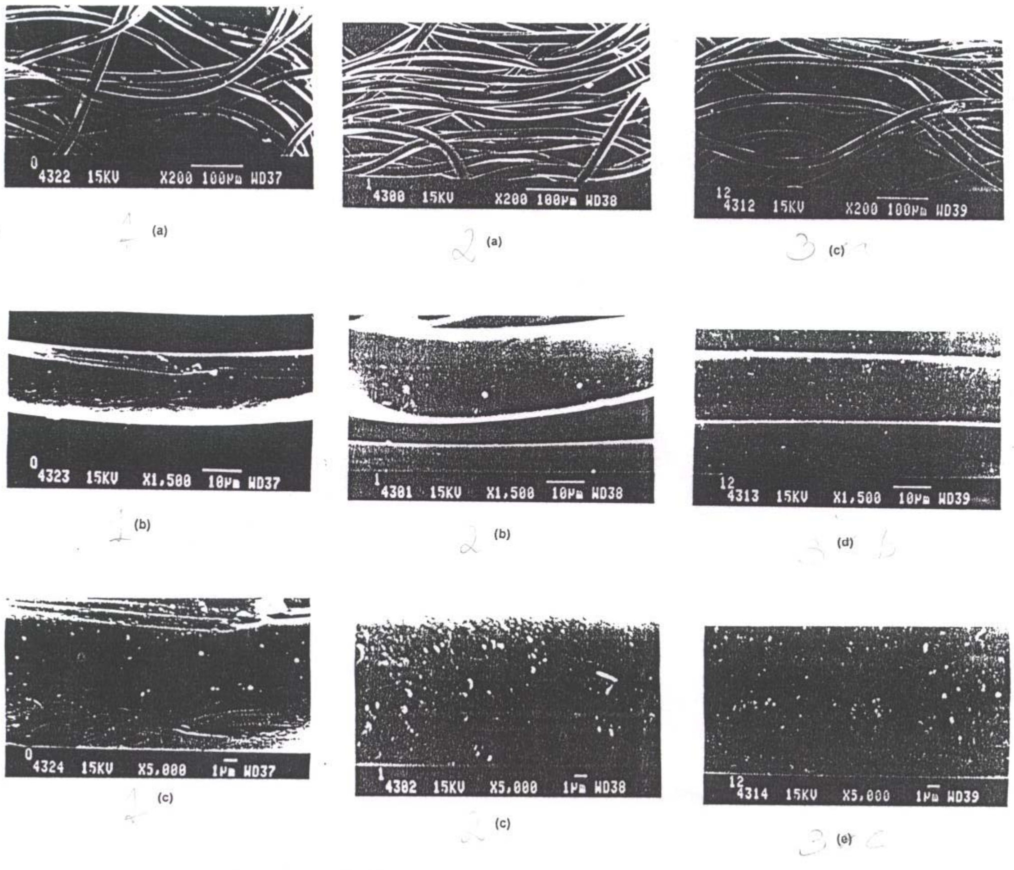

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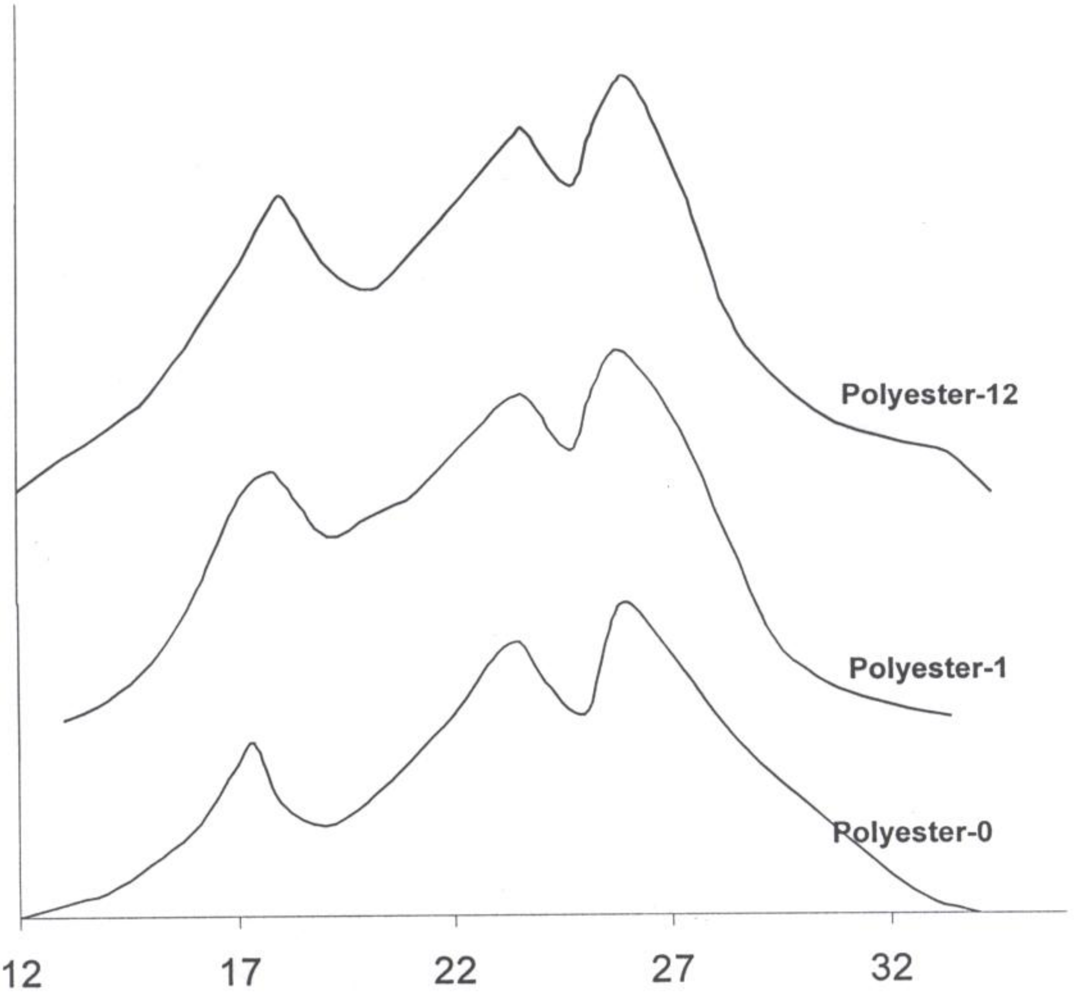

Fig. 9 *X-ray diffractogram of SAMPLE-0 , I and II denoted as polyester 0, 1 and 12 respectively.*