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GAMMA-IRRADIATION EFFECTS ON CRYSTALLINE STRUCTURE AND THE THERMAL STABILITY OF AWASSI IRAQI WOOL

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ABSTRACT

The effects of γ-irradiation (5-1000kGy) on the crystalline structure (crystallinity and crystalline size) and the thermal stability of the Awassi Iraqi wool were monitored. Wide-angle X-ray diffraction and DSC techniques have been used for this project. Using a numerical analysis method, the X-ray diffraction patterns were resolved into two peaks and background, the crystallinity was calculated to be 58.2% and showed that wool is a crystalline polymer having an α–keratine folder chain structure. No change in the lattice structure was observed as wool fibers were irradiated up to 1 MGy.

The apparent endothermic peak at 126.3°C disappeared in the irradiated samples, indicating a loss in the bound water content as a result of γ-irradiation. The endothermic peak that appeared at 235.2 °C gets broadened and shifted slightly to a lower temperature (234.8-233.3°C) for the irradiated wool sample. These thermal behaviours suggest the lower thermal stability of the irradiated wool fibers, indicating some loss in cystine content. The endothermic peak appeared at 314.4 °C showed a broader area and more flattened, and shifted slightly to lower temperature with increasing dose, concluding the greater degradation reactions and a lower stability.

خلاصة

تم في هذا البحث دراسة تأثير أشعة غاما على التركيب البلوري (درجة التبلور وحجم البلوريات) والاستقرارية الحرارية للصوف العراقي المواسي، لمدى واسع من الجرعات من 5 كيلو غري ولحد ميجاغري.

استخدمت لهذا الغرض تقانات حيود الأشعة السينية عند الزاوية الكبيرة والمسعر الحراري التفاضلي. باستخدام التحاليل العددية تم تحليل أنماط حيود الأشعة السينية إلى قمتين والى الخلفية وكانت درجة التبلور المحسوبة لألياف الصوف العراقي 58.2%. كما أظهرت هذه الأنماط أن بوليمر الصوف متبلور ذو تركيب مطوي السلسلة من نوع كيراتين α- . لم يتغير التركيب البلوري نتيجة التشعيع بجرعات مختلفة ولحد 1 ميجا غري.

أما التحاليل الحرارية فان القمة الماصة للحرارة عند درجة 126.3 سلسيوسية في منحنى التحليل الحراري التفاضلي للصوف غير المشعع قد اختفت للنماذج المشععة مما يدل على نقصان في محتوى الماء المقيد نتيجة التشعيع. أما القمة الماصة للحرارة عند درجة 235.2 سلسيوسية فقد حصل لها اتساع وتحول قليل نحو درجات حرارية اقل في المدى (234.8-233.5 درجة سلسيوسية) نتيجة التشعيع. يدل هذا السلوك الحراري على أن النماذج المشععة لها استقرارية اقل من غير المشععة نتيجة فقدانها لكمية من السيستين.

INTRODUCTION

During the last three decades there has been growing interest in the beneficial application of high-energy ionizing radiation in the industry of textiles. The radiation processing of textiles have been adequately reviewed by Mahmood[1]. The effects of gamma ionizing radiation (and neutrons or electrons) on wool fibers were studied extensively, these include, effects on the mechanical properties [2-10], alkali solubility [8-13], amino acids contents [8,9,12-14], supercontraction behaviou [5,6,15] basic elements contenst [1,8,9], dyeability [1-3,16], electrical conductivity[17], and fibre structure using infrared absorption spectroscopy [18,19]. These investigators concluded that high does of γ rays ($\geq$ 100 kGy) caused destruction of wool fibres as revealed by:

a- Decrease in tensile properties.
b- Increase in alkali solubility, dyeability and supercontraction.
c- Oxidation of cystine (especially when irradiation was carried out in air) to cysteic acid and increase in cysteine.
d- Decomposition of tryptophane and tyrosine.

Destruction at high doses was attributed to cleavage of amide links[8,18]. Cleavage of disulphide bonds [4,8,14], and breakage of secondary hydrogen bonds[15].

The wool keratin is a multicomponent fibre and consists of three main morphological components: cuticle, cortex and cell membrane complex, which consists of further subcomponents; (see fig.1) Many physical properties of wool are determined by the microfibril-matrix complex of the cortex[20-24]: partly helical, cystine poor microfibrils embedded in a nonhelical, cystine rich matrix. The wide- angle x-ray and the differential scanning calorimetry (DSC) techniques are very powerful tools for determining the structure and the structural changes of the microfibril-matrix complex.

X-ray diffraction studies[24-26] of wool fibres showed that there are two principal x-ray diffraction patterns. The α -keratin exhibited by unstretched wool fibre in which the main wool chains are coiled up in a spiral form, and the β- keratin characteristics of stretched fibre where the coil extends (α-helices into β–pleated sheets transformation)[26-28].

There is hardly any reported study on the changes in the crystalline structure and thermal stability of wool fibres as a result of irradiation. Furthermore, Iraqi wool has never been characterized by DSC nor x-ray diffractometry. The aim of the present study is concerned with DSC and x-ray diffraction examination of Iraqi wool sample irradiated at different doses of gamma photons occurred within irradiated wool fibres, and to put forward some information that may help in future research topics.

Interpretation of Wide-Ange X-Ray Diffraction Pattern

The main feature of the wide – angle x-ray pattern in unstretched wool may be summarized as follows [27] :

1- A group of strong, sharp, near meridional reflections with spaacing about 0.514 nm.
2- A weaker meridional reflection of spacing 0.15 nm.
3- A diffuse equatorial reflection or group of reflections with a mean spacing of about 0.98 nm.
4- A number of diffuse, but discrete, reflections together give the impression of an elliptical halo.
5- Such refections as occur indicate good crystallite orientation in the direction of the fibre axis.

In the range of equatorial diffraction angle with which we are concerned, there are two main components in the unstretched wool fibers. These are: the composite reflection at 0.98 nm which is due to the presence of a coiled α-helix in the wool fibre [29,30], and the board band in the region of 0.45 nm which was previously considered to be part of the non-crystalline halo[29] or as entirely amorphous scattering[27]. However,

Jakšic[31], and Jakšic and Jovanovic[30] developed a new theory proposing the existence of β-crystalline phase in the unstreched wool fibre, and the diffuse halo with broad maximum between approximately 0.40 and 0.47 nm on the equator would be caused, at least partly, by the pressence of β-crystallites . The length of these crystallites could be relatively short and small, in comparsion to the length of the ∝-helix and that of the supermolecular elements of wool structure.

It could cause a lesser degree of orientation in relation to the degree of orientation of rigid ∝-helices. In this case the degree of crystallinity is influenced by the β-crystalline form as well as ∝-crystalline form, and is assumed as the integral intensity of the tow peaks in the x-ray diffraction curve.

The diffuse background under the two peaks considered to be due to scattering form the non – crystalline regions of the fibre.

Interpretation of DSC Thermogram

The succession of events that occur when wool is heated in vaccum can be summarized as follows[32] : ordinary drying up to 120°C, removal of strongly bound water at about 130-150°C, slow formation of amide crosslinks and giass transition phenomena at for of amide crosslinks and glass transition phenomena at about 160°C, melting of a small part of the ordered phase at 215°c with the newly formed amorphous material, melting of the major part of the wool protein at 235°C, disulphide bond cleavage at 230-250°C, general pyrolysis above 250°C and a severe breadown of ppeptide chains about 300°C.

The transition that occure above 260°c is refered [33] to as liquefaction, the broad endothermic peak at 325°c was associated with melting of β-keratin and with the net heat effects from the degradation processes.

The characteristic doublet endotherm observed in the region of 220-260°C is believed [34] to relate to the thermal stability of the fibre, and many workers [33-39] have reported on the shape and nature of this doublest. It was concluded that the first endothermic transition peak at 235°C related to the microfibril is caused by an dirreversible helix unfolding (denaturation process)[22,40,41] while the second peak at 254°C is a matrix decomposition. However only some sulphur-rich (matrix-rich) keratin such as intact human hair yields clearly this peak [39,40].

EXPERIMENTAL

Materials

Scoured Awassi[42,44] Iraqi wool was obtained from the General Establishment for Woolen Industries. Random samples underwent a prolonged treatment with ethanol, this was followed by a long rinse in distilled water (24 hr), after which they were allowed to dry at room temperature and moisture. Because of the variability in wool properties within the same sample, each sample was divided, before irradiation, into two identical specimens, one was designated as a control (unirradiated) and the other was irradiated to the required dose, in order to calculate the relative values rather than the absolute ones.

Irradiation

Irradiation was carried in Canada gamma-cell-220 ^{60}Co irradiation facility located at the Agricultural and Biological Research Centre / Iraqi Atomic Energy Organization –Baghdad.

Batches of wool fibers were packaged in a small plastic containers made of polyethylene, and irradiated in the dry state at room temperature and atmospheric pressure to different doses ranging from 5 KGy up to 1 MGy in air, at dose rate around 5 KG/hr.

MEASUREMENTS

1-X-Ray Diffraction Facility .

Equatorial wide-angle x-ray diffraction traces were recorded in the reflection mode using a Philips PW 1050 diffractometer mounted on a stabilized Philips x-ray Generator PW 1729 operating at 30kv and 25 mA, Ni-filtered Cuk $\propto$ radiation was used. The diffractometer is controlled by a Microprocessor PW 1710, and incorporates Proportional Counter, Amplifier, and Pulse–height and Fulse-height Analyzer. The diffractometer contains, flat circular sample holder on which the sample can be laid and fixed, it was run in the step – scan mode at specified anagular steps ranging between o.1 and 0.5 (2θ).

The output data, comprising 2θ angle (in the range 4-60°) versus count/sec, was fed digitally to the printer, Finally the data was fed into an IBM Electronic Computer Touche 486 for analysis.

An oven-dry (at 105°C for 2 hr) test specimen of wool fibers were chopped[45-47] shortly with the help of scissors , into small pieces with powder like consistancy . A 100 gm powder of the specimen was pressed for 15 min to a disk of 2.5 cm diameter and about 1mm thickness.

The data was analysed using the multipeak resolution procedure of Hindeleh and Johnson [40-50], The intensity data was corrected for air scatter, compton scatter, polarization and Lorntz factor[51], and finally normalized to a conveniet area in the range 5-35°(2θ), then the normalized diffraction peaks were resolved in terms of combined Gaussian–Cauchy profiles for each peak, together with a polynominal background.

Peak area crystallinity is then defined as the percentage ratio of x-ray under the resolved peaks to the total x-ray scatter under the corrected normalized scan.

$$\text{Crystallinity} = \frac{\sum_{t=1}^{t} \int_{2\theta_1}^{2\theta_2} Ii(2\theta)d(2\theta)}{\int_{2\theta_1}^{2\theta_2} I(\text{norm})(2\theta)d(2\theta)} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

2- Differential Scanning Calorimetry

DSC analysis was achieved in a Mettler DSC Calorimeter Model TA 3000 controlled by a TC 10A TA Processor where the heat flow against the temperature was scanned. The following analytical functions could be performed: assignment of the peaks temperature, determination of the base line, integration of the total heat of fusion and calculation of the enthalpy.

DSC measurements were performed for oven–dry and cut[52] wool fibers (weighing exactly 6.5 mg placed in an aluminum crucible) with a heating rate of 5°C/min, from 35 to 400°C, purging 30cm^3/min of nitrogen gas.

An empty standard aluminium pan with perforated lid was used as a reference, the DSC cell calibration coefficient at the temperature of interest was found from separate measurements made on indium with heat of fusion 28.45 J/g and melting point 156.6°C. For temperature calibration, lead and zinc (meling poings 327.4 and 419.5°C respectively) were used in addition to indium.

crystallinity of unsstretched Lincoln wool[31], where 40% of crystallinity was attributed to the ∝-phase and 17% to the β-phase.

The wide angle x-ray diffraction studies showed that Iraqi wool is a crystalline material with little amount of ∝-phase 6.33-8.67%.

2-DSC Thermograms

The DSC curves for the γ-irradiated wool fibers are shown in Fig.4. Control sample (a) showed a small endotherm spanning from 118 to 146°C with a peak at 126.3°C, which is apparently due [34] to the desorption and vaporization of water in the bound state.

A shoulder–from endothermic peak is observed aat 235.2°c with a broad endothemic peak in the higher temperature range from 210 to 275°C, which is attributed, as suggested by other workers[22,39,56,57], to the helix peak superimposed by crystine decomposition reactions and various other decomposition reactions. After that the DSC curve shifted toward the exothermic reaction. The endothermic peak at 314.3°c in the range 303-342°C may be attributed to the melting of β-keratin as mentioned in the preceding paragraph.

The endothermic peak apparent at 126.3 °C disappeared in the irradiated samples indicating a decrease in the bound water content as a result of γ-irradiation. The endothermic peak that appeared at 235.2°C became broad and shifted slightly to lower temperature in the range (234.8-233.5°C) for the irradiated wool samples. These thermal behaviors suggest the lower thermal stability of the irradiated wool fibers, indicating loss in cystine content. A support to this was given earlier [22,33,34,38], where it was stated that, reduction in the number of crosslinks, especially the disulphide linkage, lower the melting point of helical regions. However, the obtained results for this endothermic peak are in agreement with the observation of other authors [55] for γ-irradiated silk fibers, except the shift of the decomposition peak at 315°c toward lower temperatures was larger compared with the present results. The endothermic peak apparent at 314.3 °C became broader and more flattened, and shifted slightly to lower temperature with increasing dose, suggesting the greater degradation reactions and lower thermal stability, this may be due to modifications involving the scission of the peptide bonds in the amorphous region.

RESULTS AND DISCUSSION

1-X-Ray Diffraction Patterns:

Fig. 2 shows normalized equatorial wide angle x-ray diffraction scans of unirradiated wool fibers resolved into two peaks superimposed on a background, the first peak at about 7.9°, corresponding to crystalline spacing (001)[53] of 1.12 nm, and the second peak at about 22.7° corresponding to crystalline spacing of about 0.39 nm. The second peak is much broader than the first one and related to diffuse reflections. These two peaks which are characteristics of the ∝-pattern of wool fibers[27] have amplitude of 7.91 and 11.73 respectively on the relative intensity scale, their angular width are 2.25° and 12.18° (2θ) respectively.

The x-ray diffraction of wool fibers remained unchanged even after irradiation with 1Mgy of γ-ray, as shown in Fig.3 suggesting that γ-irradiation did not break the crystalline lattice structure of the wool fibers.

Table 1 displays quantitavely the two peaks parameters of the unirradiated wool fibers, with their changes or their relative values (irradiated/control) as a result of irradiation with different doses of γ-ray. The crystallinities (Ap) (expressed as the percentage peak area) of the first peak indvidually and of both peaks, as well as their relative values (R) are shown. The peak position (p) of each peak and its change (Δp) as a result of irradiation are also shown. In this Tables we can see also the amplitude (A) and width (W) of each peak with their relative values (R) as a result of irradiation. Within the limit of the experimental error, the obtained results indicate that no change is observed as a result of γ-irradiation. The absence of any shift in the x-ray peaks as a result of irradiaton implies that the unit cell is not altered and that the major crystalline structure remained unchanged regardless of γ-irradiation. No remarkable change is observed in the relative peaks area or width, this indicates that both crystallinity and crystallite sizes (∝ or β), which are inversely related to the width [48,50], remained unchanged. The results of the present work are consistent with those reported for cotton fibers[54], where the crystal lattice structure of cellulose, i.e. elementary cell and crystallite sizes, was almost unaffected even at high γ-rays of 1Mgy. Our current results are also in reasonable agreement with those reported for silk fibers [55] irradiated up to 210 Kgy.

The present results for the crystallinity of unirradiated unstretched Iraqi wool fibers (as calculated from the areas of the two peaks) is in the range 47.54-65.18%. Nearly the same result (57%) was observed for

crystallinity of unsstretched Lincoln wool[31], where 40% of crystallinity was attributed to the ∝-phase and 17% to the β-phase.

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Table 1 : Peaks parameters of unirradiated wool fibers , and their relative values (irradiated/control) after different γ-irradiation doses .

Dose KGy	Peak Area (%)				Peak Position (2θ°)				Amplitude				Width (2θ°)			
	1st		1st+2nd		1st		2nd		1st		2nd		1st		2nd	
	Ap	R	Ap	R	P	ΔP	P	ΔP	A	R	A	R	W	R	W	R
40	7.55	0.911	65.18	0.953	8.00	-0.10	22.25	+0.06	7.25	0.952	13.03	0.942	2.66	0.989	14.29	0.956
200	8.33	0.972	67.54	1.0093	7.81	+0.01	22.53	+0.20	7.91	1.109	11.73	1.006	2.25	0.907	12.18	1.006
500	8.67	1.009	65.00	1.061	7.88	+0.01	23.05	-0.62	8.72	1.236	13.34	1.013	2.54	0.803	14.29	1.025
1000	7.04	0.858	55.04	0.923	7.88	-0.18	23.16	-0.64	9.42	0.911	12.04	0.985	2.03	1.192	12.30	0.925

CONCLUSIONS

In the course of the obtained results the following conclusions can be drawn :

1- Wide-angle x-ray diffractometry revealed that Iraqi wool is a crystalline polymer, and has an ∝-keratin folded chain structure .

2- No change in the lattice structure was observed as a result of γ-irradiaton up to 1MGy.

3- Thermal stability of wool fibers was slightly affected by irradiation up to 200kGy (shift in the helix peak from 235.2 to 233.5°C).

4- The x-ray diffractometry and DSC calorimetry results lead us to conclude that the effects of γ-irradiation at high doses are the cleavage of disulphide bonds and scission of the peptide bonds, as suggested earlier [1] in an explaination of the increase in alkali solubility, and decrease in tensile properties and hydrophilicity of Iraqi wool fibers.

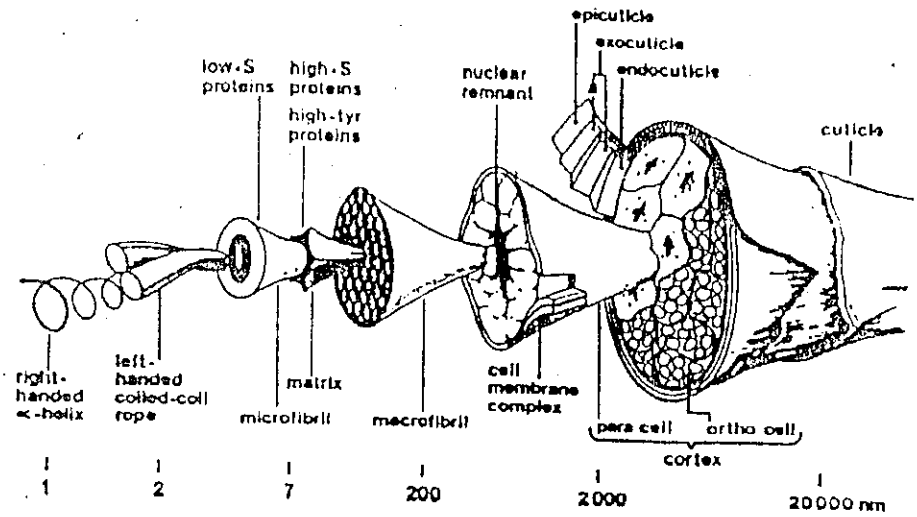

Fig. 1: Schematic diagram of the morphological components of a fine wool fibre [20].

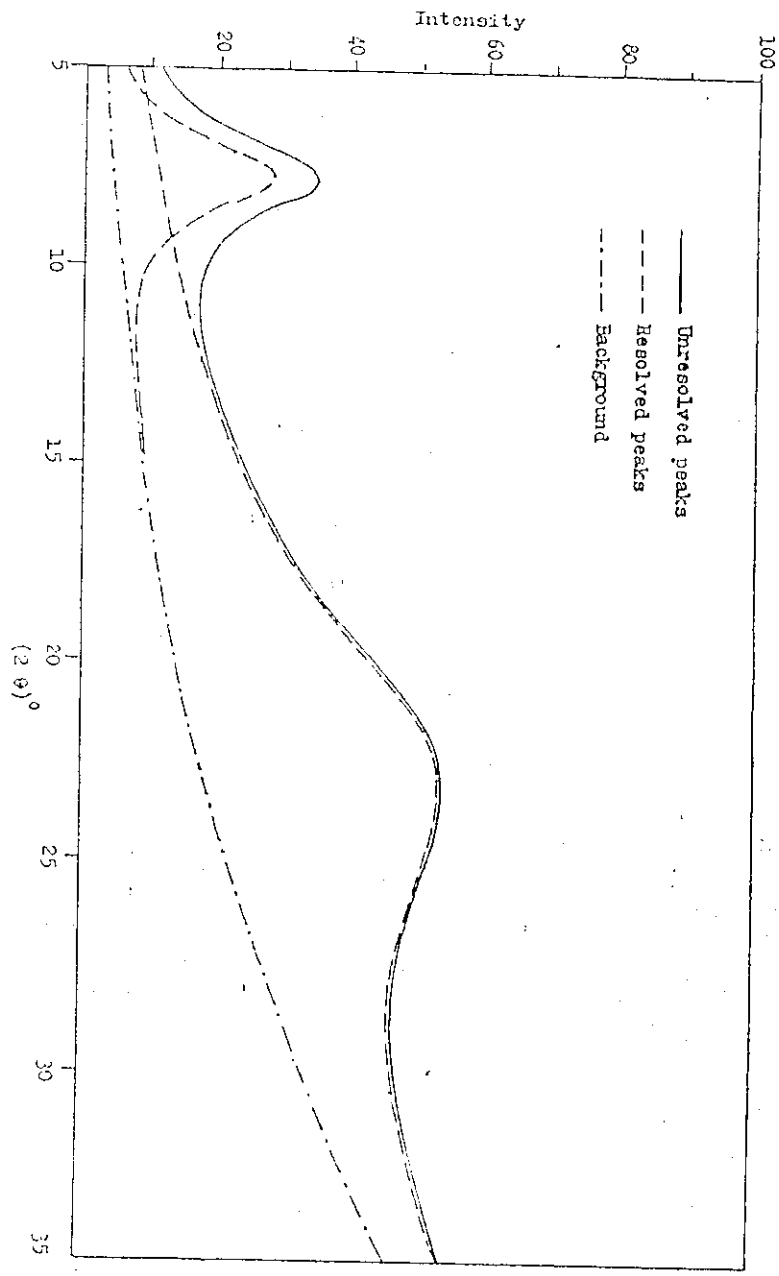

Fig. 2 : Equatorial X-ray diffraction scan off unirradiated wool fibres resolved into two peaks.

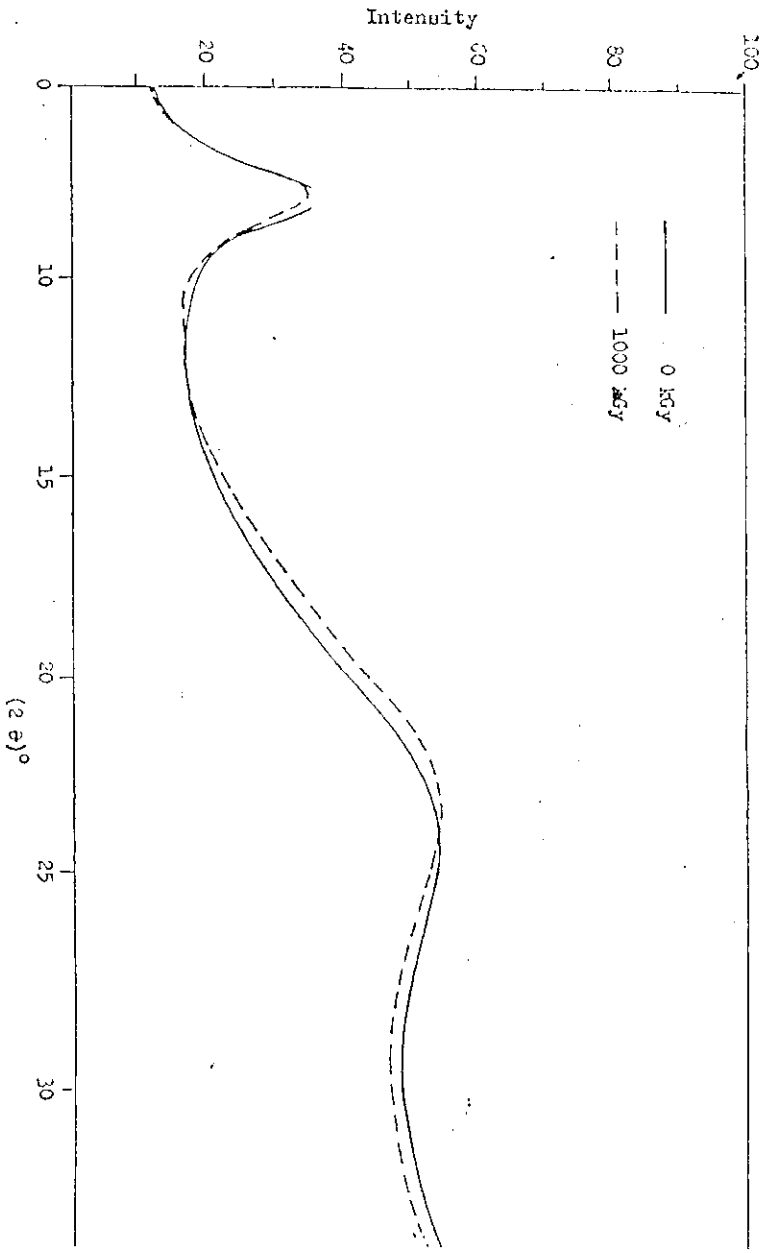

Fig. 3 : X-ray diffraction intensity curves of the control and irradiated (1 MGY) wool fibres.

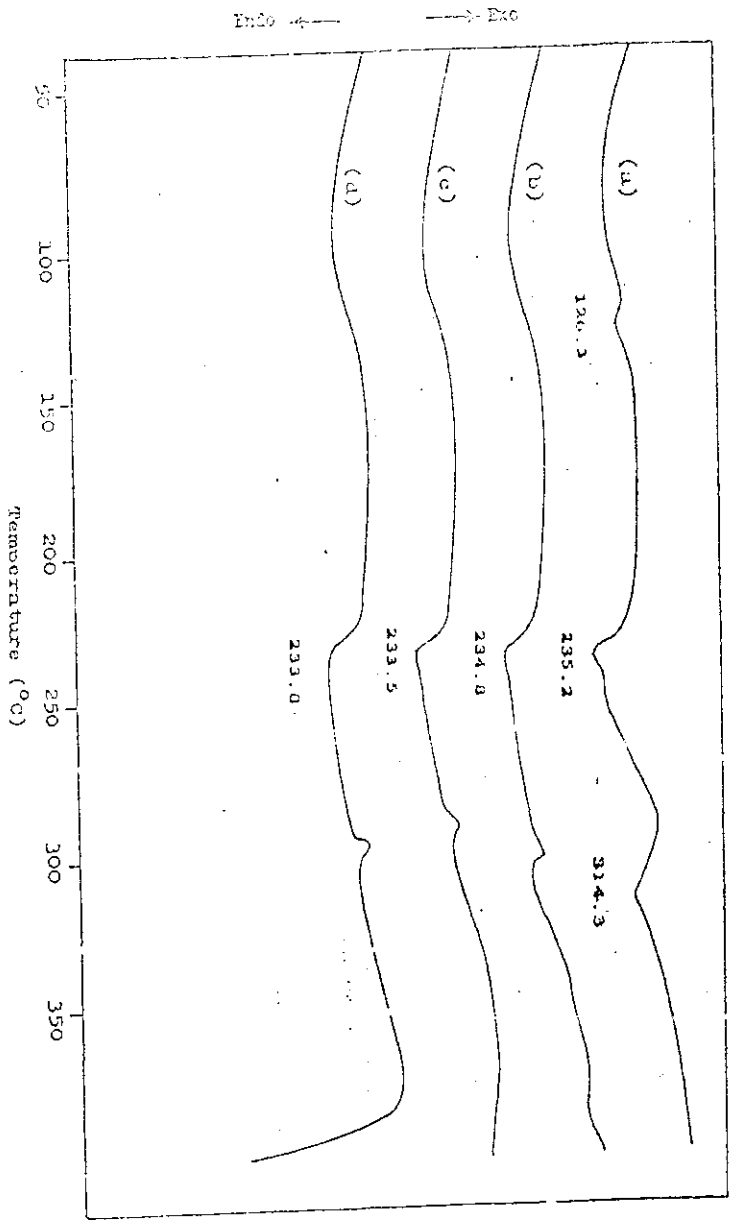

Fig. 4 : DSC curves of irradiatated wool fibres with different doses. Absorbed dose in kGy: a) 0; b) 40; c) 110; d) 200.

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