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Effects of Gamma - Irradiation on the Hydrophilicity and Optical Properties of Awassi Sheeps Wool

تأثير أشعة جاما في قابلية الامتصاص للماء والخواص الضوئية لصوف الاغنام العواسية

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خلاصة

تم في هذا البحث دراسة تأثير اشعة جاما في قابلية امتصاص الصوف للماء (محتوى الرطوبة ، نسبة الماء المقيد ومعدل الجفاف) والخواص الضوئية (فجوة الطاقة وحافة اورباخ) لصوف الاغنام العواسية لمدى واسع من الجرعات ولحد ا ميجا جري ولاول مرة . تبين ان الجرع القليلة تزيد من النسبة المئوية لمحتوى الرطوبة والماء المقيد ، بينما الجرع العالية ادت الى انخفاض في قيم هذين المعلمين ، وقد لوحظ عكس السلوك مع تغير الجرع الممتصة لمعدل جفاف الماء الحر . كانت قيم فجوة الطاقة البصرية (E_{opt}) وحافة اورباخ (E_e) لالياف الصوف غير المشععة 2.64 و 0.4 الكترون فولت على التوالي ، كما لوحظ حصول انخفاض في منحني(E_{opt}) عند الجرع القليلة ثم يتزايد بزيادة الجرع ، بينما يسلك منحني (E_e) عكس السلوك . اثبتت الدراسة ان الجرع القليلة في المدى 10-20 كيلو جري تزيد من قابلية اكتساب الياف الصوف للماء . ودل سلوك الخواص المذكورة اعلاه مع الجرع ان الترابطات العرضية هي المتغلبة في الجرع القليلة ، بينما في الجرع العالية فأن عمليات التحطم هي المتغلبة .

Abstract

The effects of γ - irradiation (0-1000 kGy) on the hydrophilicity (regain bound water content and drying rate) and optical properties (optical energy gap and Urbach edge) of Awassi sheeps wool fibres were investigated for the first time . It was found that regain and bound water content increased to their maximum values at 20 kGy then decreasing sharply as the dose increased up to 1000 kGy ; the opposite sense was found for drying rate . Optical energy gap (E_{opt}) and Urbach edge (E_e) for unirradiated wool fibres were 2.64 and 0.4 eV respectively . The curve of the former vs. dose had a depression at low doses then increased with increasing doses , while the curve of the latter changed in the opposite sense . The results showed that doses in the range 10-20 kGy favoured optimum hydrophilicity of wool fibres . The overall behaviour suggested that the crosslinking process in the dominant reaction at low doses , while at higher doses , the process was dominated by degradation .

1. 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 has been adequately reviewed by Mahmood [1] . In recent years physical and chemical modifications of the native fibres to impart new properties or to improve them have become major factors in wool industry and utilization . A new approach to the modification of wool properties is to expose its fibres in the present or absence of chemical reagents to ionizing radiation . γ - irradiation is found to have a potential interest for processes aimed at improving wool properties such as shrink and wrinkle resistance and crease retention .

The effects of γ - ionizing radiation (and neutrons or electrons) on wool fibres were studied extensively , these include , effects on the mechanical properties [2-10] , alkali solubility [8-13] , amino acides contents [8,9,12-14] , supercontruction behaviour [5,6,15] , basic elements contents [1,8,9] , dyeability [1-3,16] , electrical conductivity [17] , and fibre structure using infrared absorption spectroscopy [18,19] . These investigators concluded that high doses of γ - rays ($\geq$100 kGy) caused destruction of wool fibres which was attributed to cleavage of amide link [8,18] , cleavage of disulphide bound [4,8,14] , or breakage of secondary hydrogen bonds [15] . On the other hand , there were differences between those authors about the effects of low doses (<100 kGy) on wool fibres , some [6,9] reported that the physical properties of wool were relaively unaffected by γ - irradiation doses of this order , while others concluded that the low doses produced a slight improvement in the tensile properties [3,5,7] and evident decrease in the dye accessibility [10] of wool fibres , those changes were ascribed to the formation of crosslinking [2,3] or rebuilding [5] of some linkages at low doses before bond breakage predominanted at high doses .

There is hardly any report about the effects of γ - irradiation on the hydrophilicity and optical properties of wool fibres (neither Iraqi nor others) , furthermore , there are no previously reported measurements available in the literatures concerning Iraqi wool irradiation save one single report [20] dealing with killing the moth grubs which attacked Iraqi wool fibrs by γ - irradiation . The effects of γ - irradiation on the mechanical properties and the crystalline structure and thermal stability of Awassi sheep wool fibres were studied by the authors [21,22] . The present work is intended to ivestigate the effects on the hydrophilicity and optical properties of Awassi sheep wool fibres subjected to γ - irradiation from 10 to 10^3 kGy , the most interesting range , in attempt to determine the optimum value of doses that may impart improved properties that will prove useful in the processing of wool . The results presented here also give new information about radiation effects on wool fibres at low radiation dose levels .

2. Materials and Methods

2.1. Materials :

Scoured Awassi [23-25] 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 rins in destilled 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 indentical specimens , one was designated as a control (unirradiated) and the other was irradiated to the required dose , and the relative values rather than absolute ones were calculated , this ensured the constancy of the working conditions .

2.2. Irradiation :

Irradiation was carried out in Canadian gamma - cell - 220 ^{60}Co radiation facility located at the Agricultural and Biological Research Center / Iraqi Atomic Energy Organization - Baghdad , Iraq .

Batches of wool fibres were packaged in small containers made of polyethylene , and irradiated in the dry state at room temperature and atmospheric pressure to different doses ranging from 10 Gy up to 1 MGy in air , at a dose rate around 5 kGy/h .

2.3. Measurements :

2.3.1. Moisture Regain

The moisture regain of the control and irradiation specimens was determined under the same conditions , following the method of ASTM [26] , the two specimens (each 2±0,02 g oven - dry weight) were exposed to the atmosphere overnight [28,29] , to bring them to moisture equilibrium [27] , then weighed again ; the difference in weights would be the moisture regain expresses as percentage of weight of dry wool fibres .

2.3.2. Drying Rate

In the first series of experiments , results had shown that the behaviour of the drying rate curves was dependent on the initial regain of wool . In the subsequent experiments a regain of about 100% was chosen as the intial moisture regain for obtaining the drying rate curves . This would be a very difficult experiment to perform because of the difficulty in controlling the weight of water content required for saturation . For experimental convenience a temperature of 80 C and a drying period of 15min were chosen . It was also very important to obtain samples with the same thermal history .

The two specimens (control and irradiated) were wetted for 30 min in distilled water patted between filter papers to remove excess , interfibrillar water and then teased out well . Attempts were made for the water content to be 100% , by removing or adding a few amount of distilled water with a mocrosyringe . After being weighed in the saturation state , the specimens were dried in weighing bottles in a vacuum oven at 80 C , with the cover removed while in the oven . At the end of the drying period (15min) , the bottles were covered and removed from the oven and placed in a desiccator before weighing , inorder to avoid exposure of the specimens to the ambient air . The heating and weighing procedures were repeated until the moisture regain would reach to approximately 10% or less . At the end of the experiment , the weight of the specimens corresponded to the dry weight obtained in the usual way by oven drying at 105 C . For each period , water content was expressed as g water / 100 g dry specimen .

2.4. Optical Properties

Diffuse reflectance spectra were measured over the wave length range 380-770 nm , at 10 nm intervals , using a Philips PU 8800 UV/VIS double beam spectrophotometer [30] , fitted with PU 7908/24 integrating spheroid [31] .

Measurements were usually made relative to a white standard plaque consisting of a polytetraflourethylene powder thickly pressed onto a plastic substrate . It was desirable to have the sample so thick that further increase in thickness did not change the measurement [32] , furthermore , it was mounted on a flat black base . Before each measurement , the zero baseline (approximately 0.3% R) and the 100% R line were recorded using standard black plaque and standard white one placed in the sample position respectively .

The output in the form of a graphical chart in which the x- axis represents the wavelength (λ) , while the y-axis represents the reflectance (%R) . Data comprising points of λ and R% values have been read out of the visible display unit .

The ratios of the extinction to the scattering coefficients (K/S) were calculated from the diffuse reflectance according to Kubelka- Munk Equation [33,34] :

$$K/S = (1-R)^2/2R \qquad (1)$$

where R is the relative diffuse reflectance

3. Results and Discussion

3.1. Regain

The moisture regain of textiles is of a great industrial importance [35] ; many excellent properties of wool as a textile fibre are more or less associated with the specific bondings of wool proteins with water [36] . Fig.1 shows how the relative regain varies with irradiation dose , an intial increase is apparent reaching a maximum value (1.13 of the control) at 20 kGy , followed by a plateau in the range 200-600 kGy , then decreases to a value of 0.7 of the control at 1 MGy .

Increase in regain at low doses may be as a result of increased crosslinking in the matrix portion of protein material which can form globules . Water molecules may form an enveloping , continuous network of hydrogen bonds and the proteins acting as a filler within this network , which might interact with the network , at the globule surface [37] . Our previous studies of the effects of γ - rays on other properties of Iraqi wool fibres supported the formation of crosslinking at low doses as revealed by a decrease in dyeability and alkali solubility [1], and an increase in tensile properties[21], in the range (10-20 kGy).

The behaviour of regain at high doses can be ascribed to the damage of the polypeptide groups that cause a reduction of the amide groups which attract water strongly, or to the decrease in the side - chain groups which attract water strongly, or to the decrease in the side-chain groups which would be involved in polar bonds.

To the best of our knowledge, there are no similar studies on the effect of γ - rays on the regain of wool fibres, except one report [8] where a decrease in water vapour sorption was observed for non-Iraqi wool irradiated with 100 kGy γ - rays, this coincides with our results at this dose.

3.2. Drying Rate

The drying rate curves of Awassi sheep wool irradiated with different doses are presented in Fig.2. The ordinate represents the percentage of water content on a dry basis. For the purpose of comparison, these curves were normalized at zero time, the shape is the same for all curves but having lower values with increasing dose. The curve of the unirradiated sample in this Fig. shows that the rate of drying is constant if the water content is more than 35%, this can be explained by the evaporation of the free water, below this value it begins to fall due to the removel of bound water. The best fit for this curve was obtained using a polynomial regression, and represented by the following equation:

$$w(t) = 1.0106 - 0.0109\,t + 2.7\times10^{-5}\,t^2 \qquad (2)$$

where w(t) is the normalized percentage water content, and t is the time.

From each curve the drying rate of free water and the percentage of bound water (based on dry weight) were obtained following the method described by Low et al. [38], the drying rate of free water was determined from the slope of the linear portion of the curve, the percentage of bound water was calculated at the limit of constant drying rate of the curve. This limit was determined as the change - over point at which the falling curve rate begins (obtained by extrapolating the linear portion of the curve). However, to obtain the actual value, the normalized slope and the percentage bound water were multiplied by the initial regain of each curve.

The variations of the relative percentage bound water and drying rate with doses of γ - rays are presented in Fig.3. The two curves are similar to each other

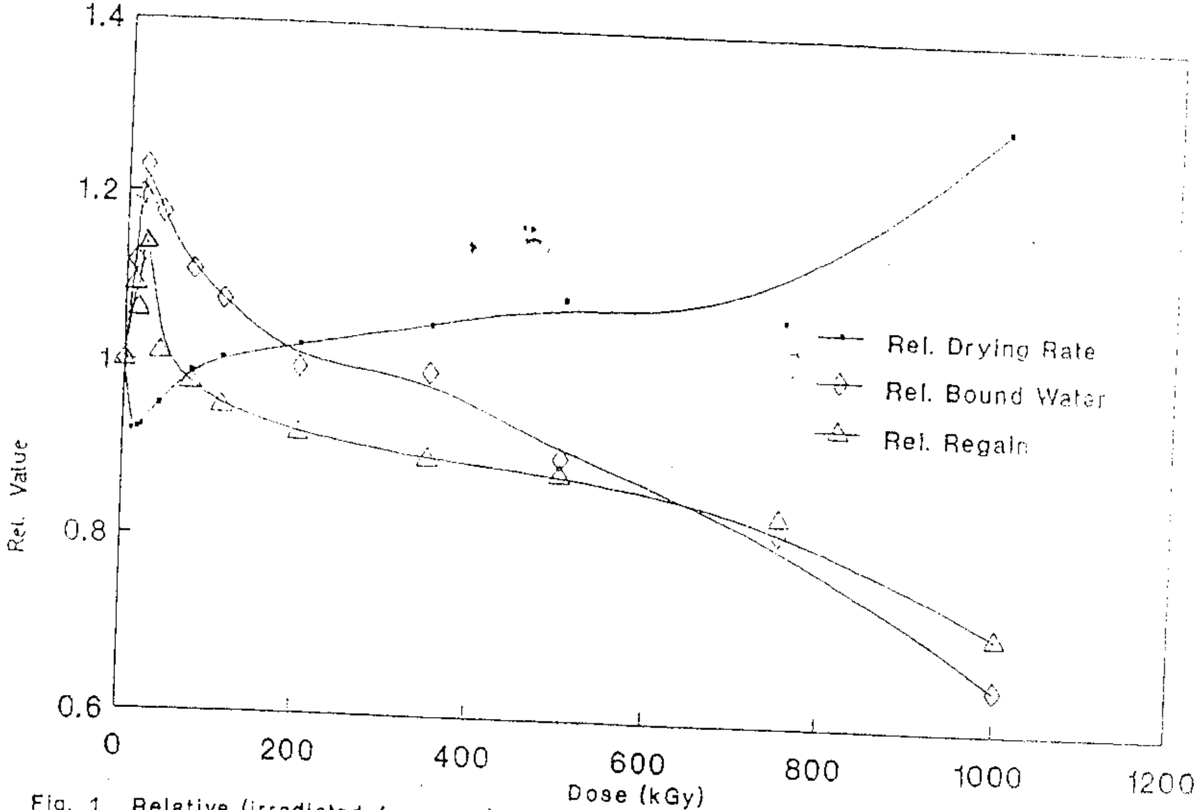

Fig. 1 Relative (irradiated / control) regain , bound water content and free water drying rate of wool fibres vs. dose

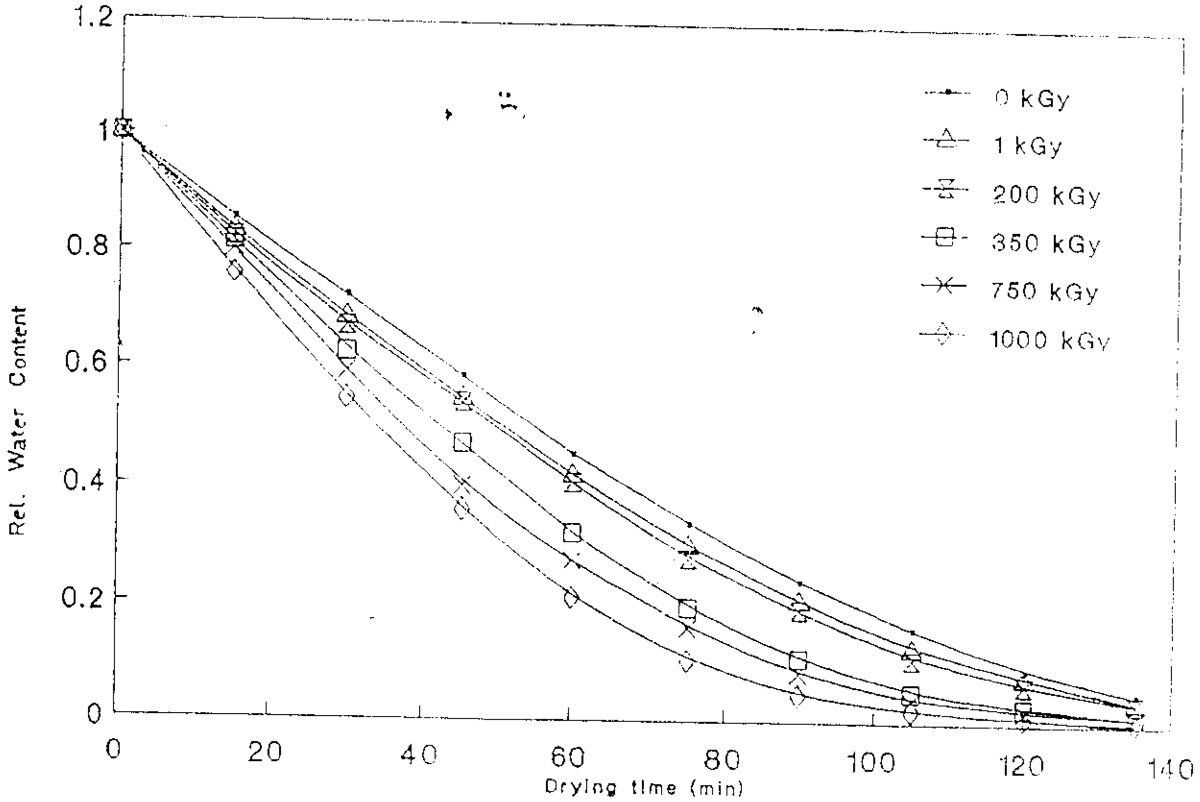

Fig. 2 Drying curves of wool fibres irradiated with different doses of γ- rays

as a mirror , as usual . when the water repellency increases , the bound water content decreases and the drying rate of free water increase , and vice versa . However , the curve of the bound water is almost coincident with that of the regain .

The behaviour of the above two parameters at low and high doses can be explained as that of the regain , where wool fibres retain the maximum amount of bound and free water at nearly 20 kGy , this can be attributed to crosslinking . Water retention decreases with increasing dose as a result of peptide cleavage and reduction in polar groups of side-chains .

3. Optical Properties

The spectral reflectance curves of unirradiated and irradiated wool samples are shown in Fig.3 , not all obtained data are presented here , data were chosen to illustrate the various shapes of the reflectance curves for wool samples irradiated with different doses . As shown in this fig. the effect of γ - rays is found to decrease the reflectance of wool fibres .

Fig.4 shows the relation between the parameter K/S and the absorbed energy for unirradiated and some irradiated samples , values of K/S were calculated from Eq.1 . The estimated values of the optical energy gap (E_{opt}) obtained from the extrapolation of the linear part of the curves to K/S = 0 as explained by Al-Ani et al. [39] , were plotted against γ-rays dose and shown in Fig.5 .

Fig. 6 shows ln K/S as a function of the absorbed energy for the same samples , the linear relationship at high photon energies indicated that wool material obeys Urbachs law [39] , but the sample do not show sharp edges , as is consistent with their amorphous nature . The values of Urbach edge (Ee) derived from the slopes of these curves were plotted against dose and shown also in fig.5 , values of Urbach edge indicate the width of the tails of localized states in the band gap region of the samples .

Variations of E_{opt} and E_e with dose seem to be opposite to each other as a mirror , their behaviour indicates that significant chemical changes are introduced in the wool fibres as a result of γ - irradiation . Actually , there have been no previous report dealing with the effect of γ - rays on these two parameters , so that a comparison is not being made

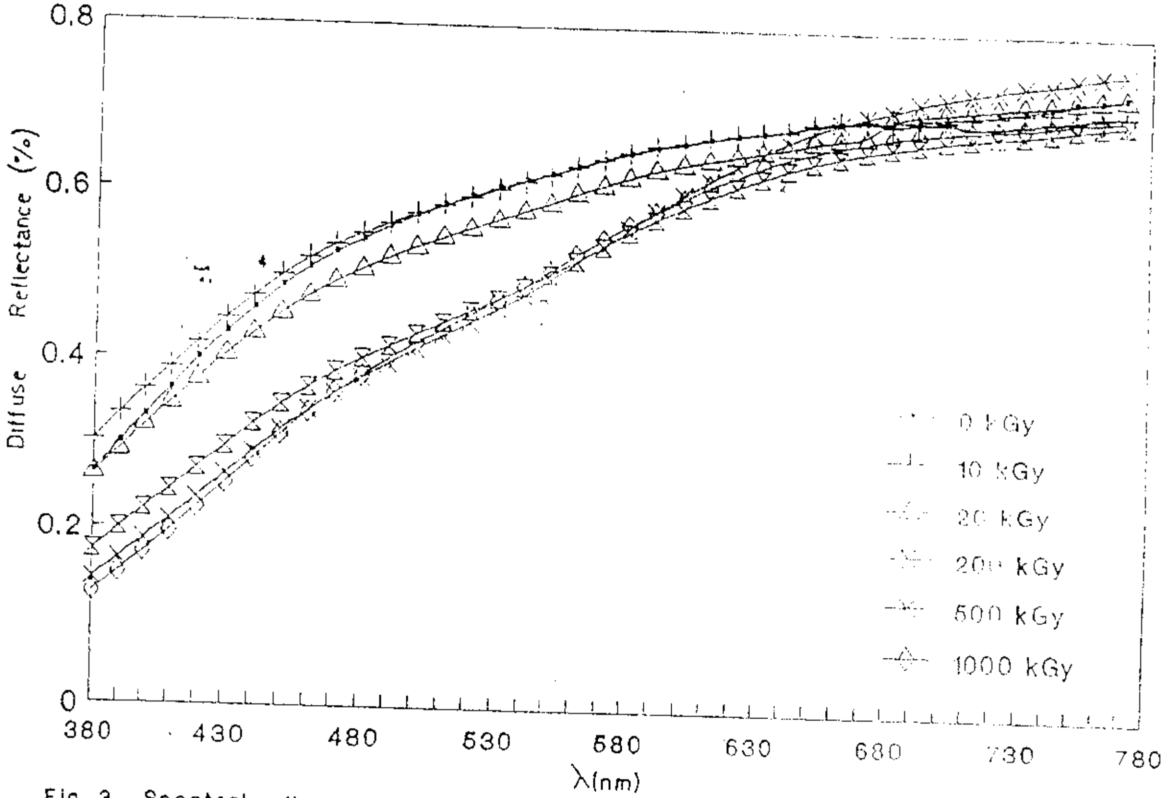

Fig. 3 Spectral reflectance curves of undyed wool fibres irradiated with different doses of γ- rays

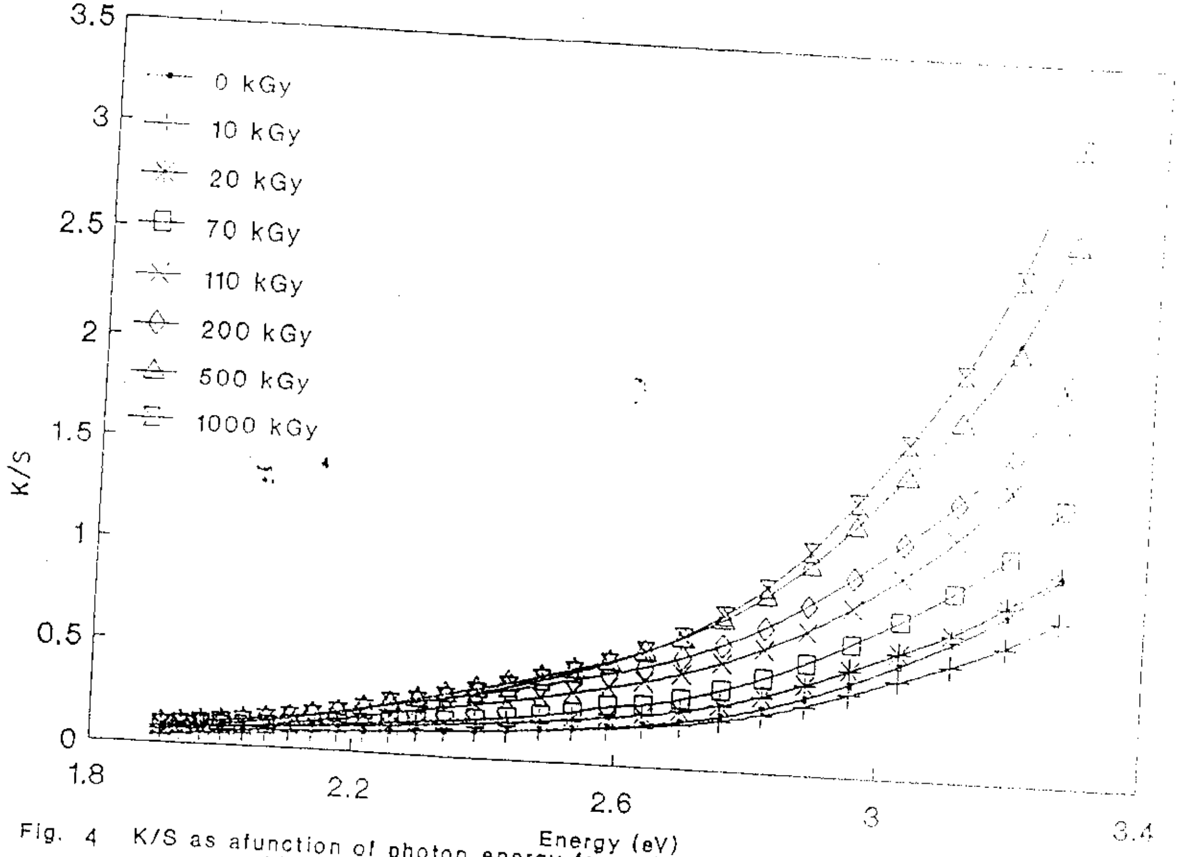

Fig. 4 K/S as afunction of photon energy for undyed wool fibres irradiated with different doses of γ- rays .

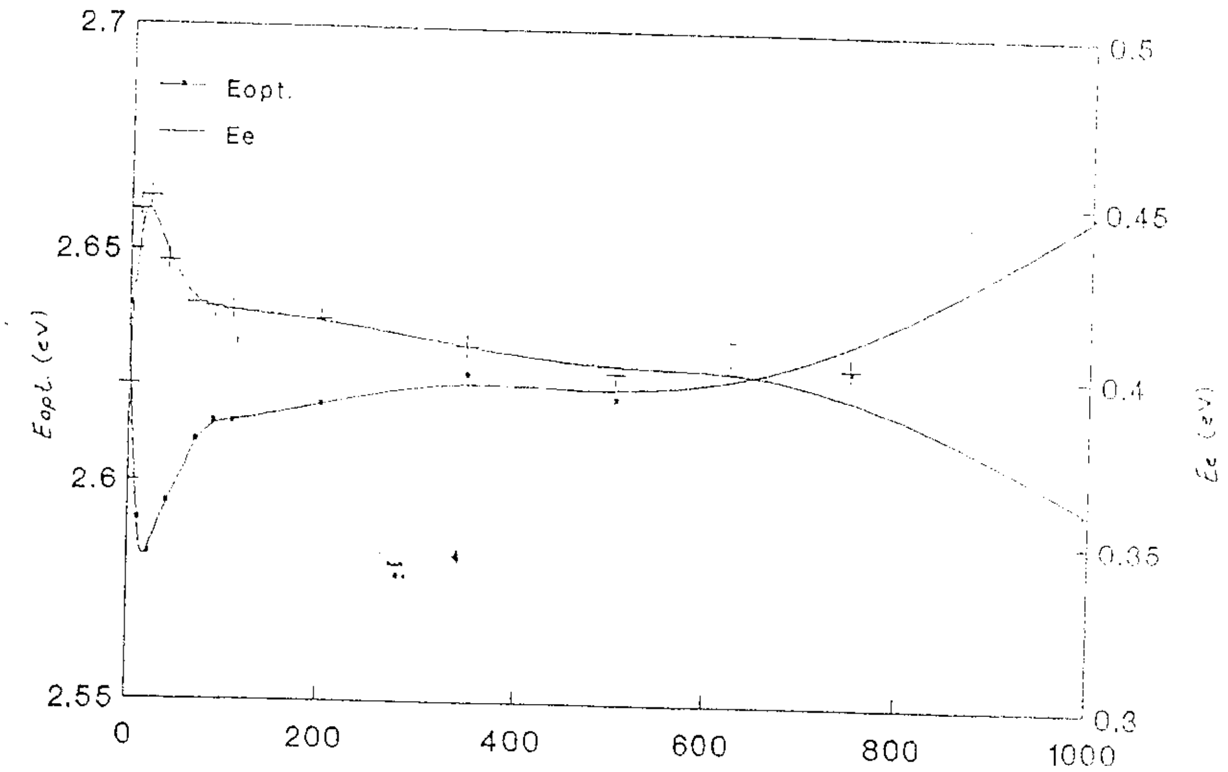

Fig. 5 Relashionship between optical energy gap (Eopt.) , Ürbach edge (Ee) and dose for undyed wool fibres .

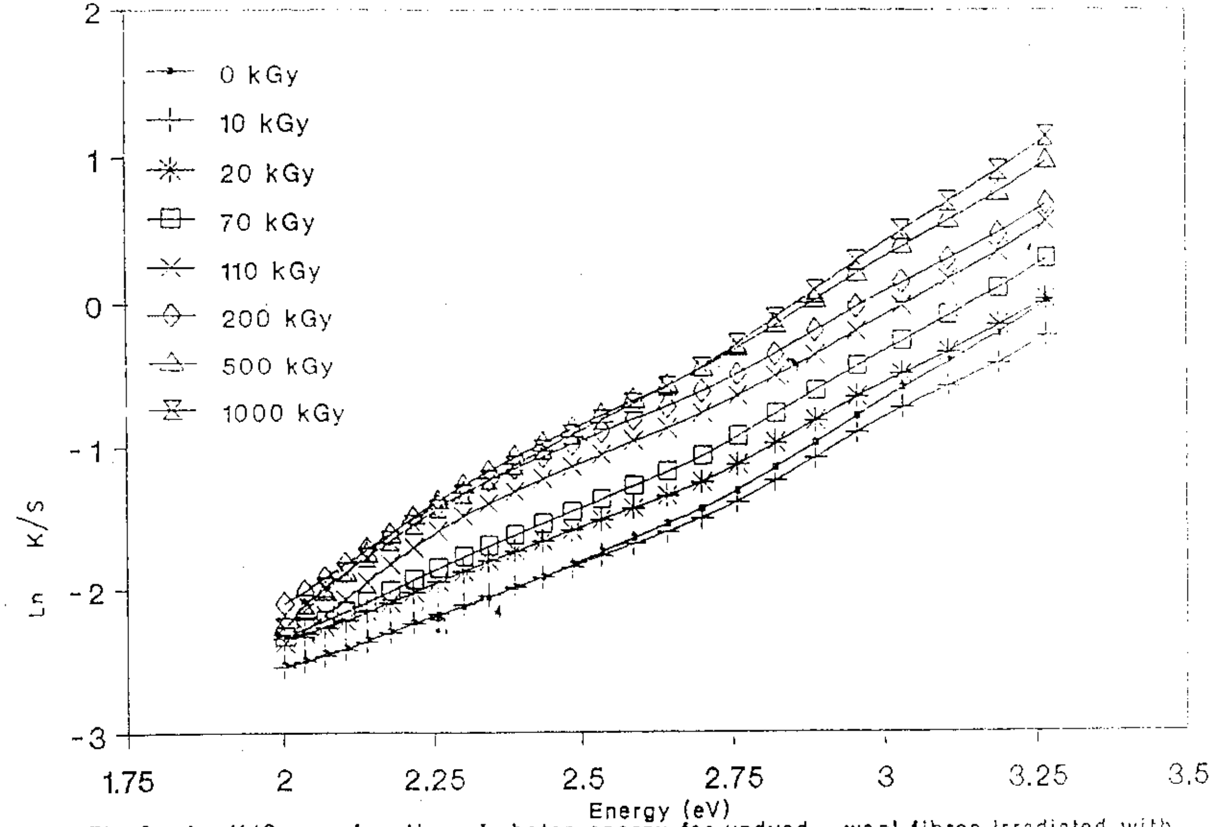

Fig 6 Ln K/S as a function of photon energy for undyed wool fibres irradiated with different doses of γ- rays.

Conclusions

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

1. Irradiation at low doses (10-20 kGy) increases the hydrophilicity of wool fibres , while at high doses , a decrease in this property was observed with increasing dose .
2. Irradiation with 20 kGy can be considered as the optimum condition that increases the hydrophilicity of Iraqi wool fibres , this increase affects the processing and finshing of yarns and fabrics , prevents the accumulation of charges of static electricity , increases the thermal conductivity and decreases the inflammability of wool .
3. Changes that occur in values of E_{opt} and Urbach edge (E_e) as a result of γ - irradiation indicate that γ - rays introduced significant chemical and structural changes in the wool fibres . Such parameters have not been previously reported for wool and are useful for characterization .

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