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**EFFECT OF GAMMA RAYS ON THE PHYSICAL AND
MECHANICAL PROPERTIES OF HIDE**

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A B S T R A C T

Effect of gamma rays on the physical and mechanical properties of hide . The effect of γ -rays on the physical and mechanical properties of hides has been studied in these experiments, using the Gammacell 220 as an irradiator. The determination of the physical and mechanical properties of the irradiated hides was carried out by Balai Penelitian Kulit (= Leather Research Institute) at Yogyakarta. Experiments show that up to a certain dose of irradiation, favourable effects can be obtained, while higher doses impair the physical and mechanical properties of the leather raw materials.

INTRODUCTION

The term radiation processing involves the use of ionizing radiation from an accelerator or radioisotope source with the ultimate purpose to obtain materials which properties are better than that which are not irradiated. [1]

The fact that food, hide, wool, etc can be sterilized by means of γ -rays is well known and has been often studied. Research in radiation chemistry concentrated on radiation-induced polymerization, radiation-induced graft copolymerization, as well as radiation-modification of plastics has been much carried out in many countries. Polymers obtained by radiation process have some advantages over those produced by the conventional chemical process. The outstanding characteristics of radiation-induced polymerization are that the initiation reaction takes place in any phase at any temperature and pressure without any catalyst, and that the polymers obtained are of high purity. [2]

In this work the influence of γ -rays on the properties of hides is presented. Animals hides are natural polymers so that it could be expected that the influence of γ -rays on them will be the same as that on other polymers.

THE ANATOMY OF THE SKIN

The skin which is a protective covering of the body of mammals, is formed by the intimate junction of two tissues, a superficial layer, the epidermis, and a deeper layer, the corium (dermis

or derma). The avascular epidermis provides the covering of the body and from it arise the hairs, the nails, and several varieties of glands, possesses many collagenous and elastic fibril. In the corium are also found a considerable amount of fat, the blood vessels, the lymphatics of the skin and it contributes connective tissues sheats to the hair follicles and the skin glands. [3,4]

In connection with the experiments presented here, only the two layers of the skin, the epidermis and the corium will be considered.

MATERIALS AND EQUIPMENT

The hides used in the experiments were supplied by Balai Penelitian Kulit (Leather Research Institute) at Yogyakarta.

The Cobalt Unit Gammacell 220 was used as an irradiator of the γ -rays.

The determination of the physical and mechanical properties of the irradiated leather raw materials was carried out by Balai Penelitian Kulit mention above.

EXPERIMENTAL PROCEDURE

The leather raw materials were cut according to the test required. The samples were irradiated with γ -rays at different doses. The tensile strength and tensile stretch of the irradiated samples were determined using an ordinary tension testing machine, Zwick & CO Kg Eisingen bei Ulm/DONAU Germany Prufmaschinen.

Fig. I and Fig. II show the tensile strength and tensile stretch respectively of the irradiated samples at various doses.

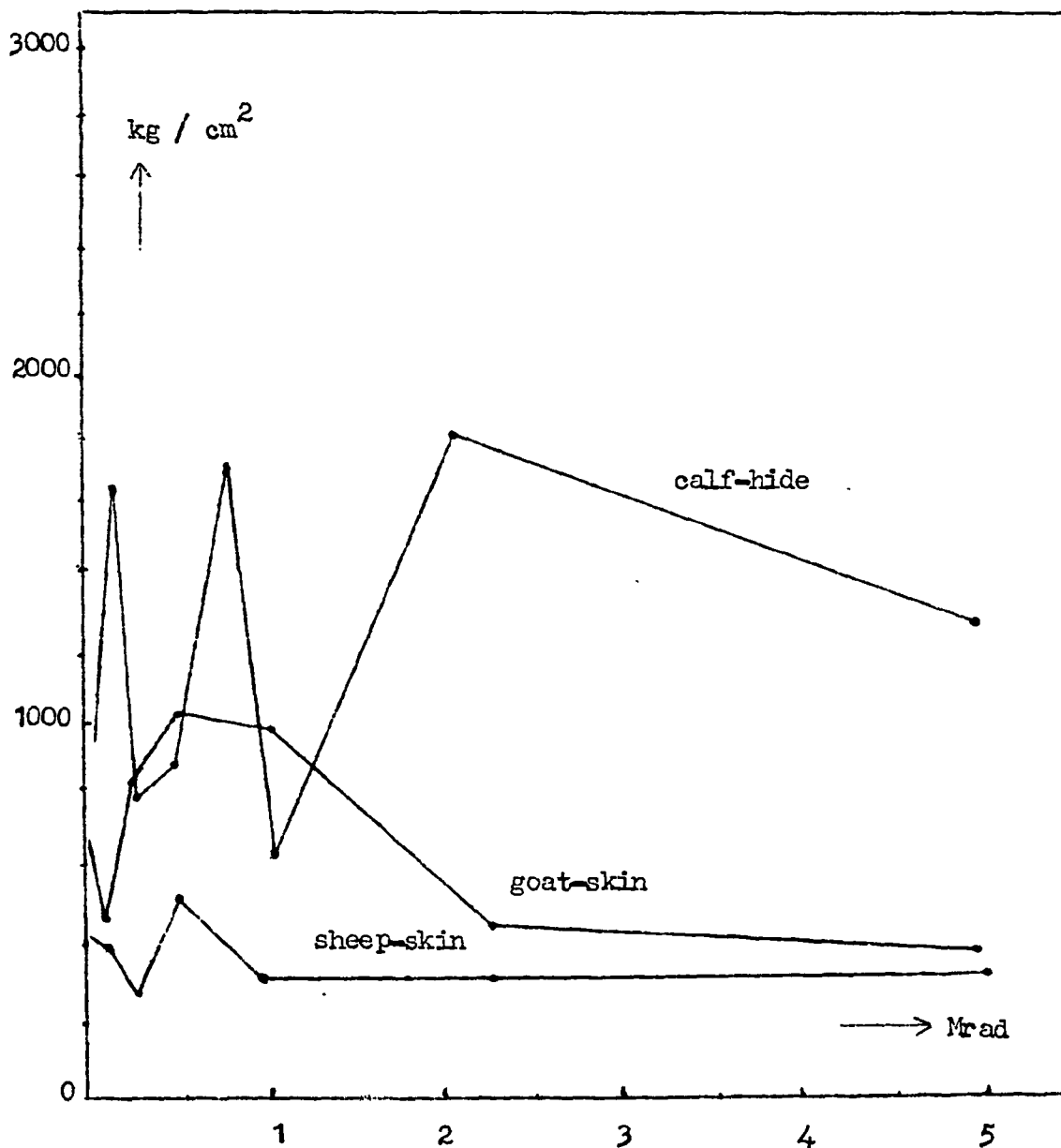
DISCUSSION

Since the change in the physical and mechanical properties of the irradiated hides and skins is a direct consequence of the absorption of energy from the γ -radiation, some knowledge of the processes by which radiation interacts with matter is essential.

Gamma-rays are electromagnetic radiation of nuclear origin with short wavelengths in the region of 3×10^{-9} cm to 3×10^{-11} cm or in terms of energy this wavelength range becomes approximately 40 kev to 4 Mev. The Co-60 used in these experiments gives equal numbers of γ -photons of energy 1.332 Mev and 1.173 Mev and tends to lose the greater part of its energy through a single interaction. The results is that a part of the incident γ -rays is completely absorbed by the irradiated samples. The various processes of absorption of γ -photons by the matter are the photoelectric effect, the Compton effect, pair production, coherent scattering, and photonuclear reactions. [5]. Only the first two of these processes are the most important in connection with the experiments discusses here.

Low-energy γ -photons are absorbed mainly by photoelectric absorption. In this type of interaction the entire energy of the γ -photon E_o , is transferred to a single atomic electron, which is ejected from the atom with an energy equal to the difference between the photon energy and the binding energy E_s of the electron in the atom, $E_e = E_o - E_s$. Photoelectric absorption is most probable for

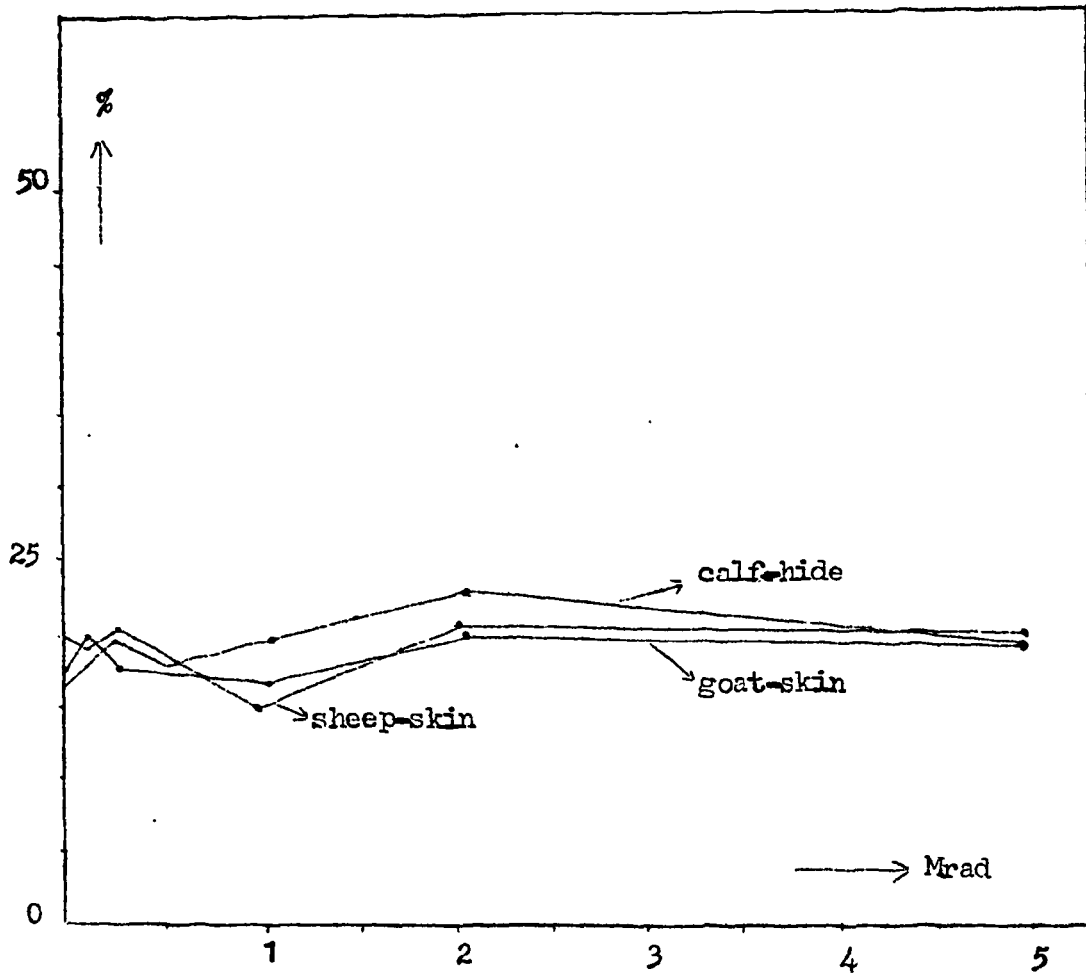
Fig. I



The tensile strength of irradiated calf-hide, goat-skin, and sheep-skin in relation to the absorbed dose.

The samples are irradiated with γ - rays.

Fig. II



The tensile stretch of irradiated calf-hide, goat-skin, and sheep-skin in relation to the absorbed dose.

The samples are irradiated with γ - rays.

high atomic number materials and for low photon energy.

In the Compton effect a γ -photon interacts with an electron, which may be loosely bound or free, so that the electron is accelerated and the γ -photon deflected with reduced energy. The energy of the recoil electron is equal to the difference between the energy of the incident and scattered photon, $E_e = E_0 - E_s$. Compton interactions predominate for photon energies between 1 and 5 Mev in high atomic number (high Z) materials and over a much wider range of energies in low - Z materials.

It is important to note that at least one electron is associated with each interaction. Thus the γ -rays lose their energy when passing through matter either by ionization or by excitation of the atoms through which they are passing. The energy lost of these moving γ -photons in matter gives rise to a trail of excited and ionized atoms and molecules in the path of the γ -photon. Excited states are produced when bound electrons in atoms and molecules of the stopping material gain energy and are raised to higher energy levels, while ions are produced when the energy gained is sufficient such, that electrons are expelled.

So the over-all result of the absorption of the γ -photon energy by matter is thus the formation of tracks of excited and ionized species. However, radiation of different types and energy will lose energy in matter at different rates, and consequently will form tracks that may be densely or sparsely populated with the active species. The differences observed in the chemical effect of differ-

ent radiation-- differences in the quantities, proportions, physical, and mechanical properties of the irradiated product-- stem from the difference density of the active species in the γ -photon tracks.

Electrons ejected as a consequence of the ionization produced by γ -radiation may themselves be sufficiently energetic to produce further ionization and excitation. The secondary ionizations that they produce will be situated close to the original ionization, giving a small cluster or spur of excited and ionized species.

Once the electrons have slowed down to thermal energies they will probably either neutralize a positive ion directly or add to a neutral molecule to form a negative ion, which subsequently neutralizes a positive ion.

Hides and skins consist mainly of high-molecular-mass proteins with a percentage content of collagen, elastin, and albumin (dry basis) of about 93 - 98 %. The vast experience accumulated by chemistry shows that with increasing molecular mass the physicochemical changes of the molecules of chemical compounds decreases. Various transformations of low - and high - molecular compounds alter the properties of the chemical compounds involved, i.e., are accompanied by energy changes and mass transfers.

The molecule of high - molecular - mass compound is composed of hundreds and thousands of atoms bound together by ordinary valence forces. Such - high - molecular - mass compounds are called high-molecular-mass polymers or simply polymers, as distinguished from monomers, which are the simple molecules that unite to form

large polymeric molecules.

The proteins which are the main constituents of hide and skin are natural polymers. These polymers are composed of α -amino acids joined with amide bonds. When studying the structure of a polymeric macromolecule, besides determining the chemical structure of its monomer units, their alternation, and spatial arrangement, it is important to establish the geometrical shape of the macromolecule. According to the shape of their macromolecules polymers fall into linear, branched, and crosslinked polymers, as illustrated schematically in Fig. III.

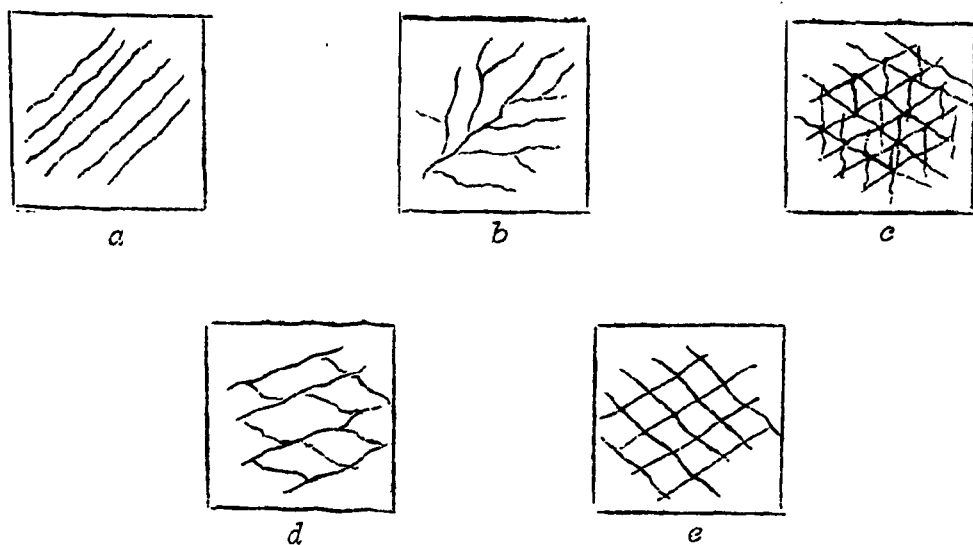


Fig. III. Schematic representation of the structure of linear (a), branched (b), and crosslinked or network polymer (c, d, and e).

In synthesis of branched polymers, branches of different monomer species can be grafted onto the linear chain of a polymer. Such branched polymers are referred to as graft copolymers.

All linear and branched polymers can be transferred into the molecularly dispersed state, e.g. on sufficient dilution of their solution, because these polymers are composed of macromolecules connected by intermolecular or van der Waals forces, the energy of which is only one-tenth to one-fiftieth of that of chemical bonds.[6,7]

In crosslinked polymers the macromolecules are bridged by chemical crosslinks. That is why space polymers cannot be dissolved or melted by heating.

Proteins are high - molecular - mass compounds whose main chain is composed of two or more different elements, e.g., carbon, oxygen, nitrogen, and sulphur, and constitute the class of heteropolymers. The properties of protein and its functions in the organism are closely related to its spatial structure, which, in its turn, depends on the amino-acid composition of the peptide chains and the sequence of the amino acids along the chain. The protein macromolecule contains one or several peptide chains linked to one another by chemical crosslinks, mostly through sulphur. To build up the spatial structure of protein the peptide chains must assume a definite configuration, fixed by hydrogen bonds. As more and more hydrogen bonds form, the peptide chains curl up into helixes. The three-dimensional structure of protein is fixed by the interaction of the π -radicals

of the amino acids to form disulphide bridges or other chemical or physical bonds. Depending on their three-dimensional structure, all proteins fall into two large classes : fibrous or fibrillar and non-fibrous or globular.

The polypeptide chains of fibrillar proteins have the shape of a helix fixed by intramolecular hydrogen bonds situated at points along the chain. Fibrillar proteins are sparingly soluble or altogether insoluble in water. When dissolved in water they form very viscous solutions.

Fibrillar proteins include the proteins contained in skin, wool, horn, feathers, and tissues. Collagen, the basis of sedimentation tissues and cutaneous coatings, occurs in hide and skin, and is an fibrillar protein.

The three-dimensional structure of protein is studied by various physicochemical methods, of which X - ray diffraction has been found the most effective.

For low - molecular - mass compounds a change in molecular mass always infers a new substance and is accompanied by a marked change in properties. But, with increasing molecular mass the difference in physical and mechanical properties of individual members of a polymer smoothes out, as it were, the monomers lose their individuality. As a result of this, the molecular mass of polymers is a statistical average. After the molecular mass of a polymer reaches a certain value it loses its significance as an index determining most of the physical properties of the substance. The average mole-

cular mass of a polymer cannot characterize its properties unambiguously, because different polymer samples with the same average molecular mass may contain different amounts of individual polymer-homologues.

A characteristic feature of the polymer chemistry is that the smallest unit participating in a reaction of a physicochemical process is not the molecule, like in classical chemistry, but the monomeric unit, or the chain section, called segment. Linear polymers, for example, when stretch out the individual segments of the chain are so far removed from one another that their mutual influence is negligible. This gives rise to specific features in the properties of polymers in their deformation. The results of physicochemical deformation of polymers must therefore be estimated statistically.

Macromolecular reactions of polymers include intermolecular reactions resulting in the formation of chemical bonds between the macromolecules and the transformation of linear polymers into three-dimensional ones, and chemical degradation of polymers, caused by chemical agents or radiation.

In reactions of intermolecular bond formation the participants are a polymer macromolecule, on the one hand, and a molecule of a low-molecular-mass compound, on the other, the molecular mass of the latter being hundreds or thousands of times smaller than that of the polymer. For example, only one atom or one monomer is needed to form a chemical bond between two linear polymers. These two lin-

ear polymers become three-dimensional in structure, as a result of which the physical properties of the system are changed markedly. This is one of the important features in polymer chemistry, because the properties of polymers depend greatly on the shape of their macromolecules. For instance, the macromolecule of a linear polymer, may approach a stiff rod in shape or may assume the shape of a helix or a coil. Depending on the shape of their macromolecule, linear polymers may differ considerably in properties. One of the good mechanical properties of linear polymers is their considerable tensile strength which is mainly due to the fact that their macromolecules can attain a high degree orientation relative to one another and are capable of very dense packing, which gives rise to numerous intermolecular bonds with a high total energy.

The physical and mechanical properties of branched polymers depend on the degree and type of branching. Branched polymers with a relatively small number of side chains are very close in properties to linear polymers. The tensile strength of highly branched polymers is lower than that of the corresponding linear polymers of the same species.

Crosslinked polymers differ greatly in properties from linear and branched polymers, due to the fact that in crosslinked polymers strong chemical bonds predominate between the macromolecules. Their physical and chemical properties depend on the number of these chemical bonds and on the regularity of their arrangement. With increasing number of these chemical bonds the polymer becomes

harder, and its tensile strength decreases.

When irradiated, a polymer may pass from one state into another. Depending on the rate of application of the radiation, one and the same polymer can be transferred from an high elastic state to the viscofluid state or to the glassy state. Hence the physical state of polymer is attributable not only to the nature of their intermolecular interactions and to ordered or disordered arrangement of their particles, but depends also on the rate and duration of the application of the external forces.

Whereas phase transformations are fully determined by purely thermodynamic variables, the transitions of polymers from one physical state to another depend substantially on non-thermodynamic variables, primarily on the dynamic of deformation.

For the practical usage of polymer materials, their mechanical properties are very important, primarily their elastic properties and strength. All the changes of the mechanical properties are related to the complex processes of regrouping of chain macromolecules and their bundles, occurring when thermodynamic equilibrium is disturbed by the action of mechanical stresses or radiation. Also deformation of polymers gives rise to an oriented arrangement of both chain molecules and their bundles.

Under the influence of ionizing radiations leather raw materials as natural polymers, undergo profound chemical and structural changes affecting all their physicochemical and mechanical properties as well. By controlling the intensity of the irradiation,

the properties of the leather raw materials can be altered as desired. The nature of the processes occurring under the influence of high-energy radiation depends greatly on the type of the leather raw materials. Under the action of ionizing radiation, such as γ -rays, the macromolecules of the leather raw material may break up into free radicals through rupture of C - C, C - H, and other bonds. This results in poorly mobile macroradicals, which decompose forming a molecule with a double bond or recombine into a three-dimensional structure. Irradiation of polymers is accompanied by the formation of double bond. Degradation and formation of three - dimensional structures always occur simultaneously when polymers are irradiated, but the rate ratio of the two processes may differ so greatly, depending on the chemical structure of the polymer and on the intensity of the radiation.

Polymers containing a quaternary carbon atom predominantly undergo degradation when they are irradiated, because several bonds open at once at the quaternary carbon atom. [6]. Some of the macroradicals formed by irradiation of the polymer may be entrained by the monomer-units and exist for a fairly long time, ranging from a few minutes to several months, depending on the type of the macroradicals.

The exposure dose necessary to cause structural change in the leather raw materials depends on the chemical structure of these materials. According to the work done by P.I. Livenko [8], formation of the structure is predominant against destruction when leather raw

materials are irradiated with a dosage of 0,1 Mrad. The physical and mechanical properties of the leather raw materials are spoiled by irradiation of them at dosage over the 5 Mrad. Deterioration of the properties of the irradiated samples is directly proportional to the increase of dosages. Fig. I and Fig. II show the changes of tensile strength and tensile stretch in relation to the absorbed dose of the γ -rays. As can be seen from these figures the tensile strength as well as the tensile stretch of the calf hide increases at lower dose, up to about 0,1 Mrad, which may be due to reorientation of the macromolecules of the hide. By increasing of the absorbed dose, cross-linking between the polymers increases proportionally which gives rise to decreasing of the tensile strength and tensile stretch of the hide. When the absorbed dose reaches about 2 Mrad, breaking of the bonds begins, resulting in the slowly decreasing of the tensile strength and tensile stretch. Increasing of the absorbed dose brings about the degradation of the hide. In case of sheep-skins and goat-skins the changes of tensile strength and tensile stretch occur at different dosages than that of calf hide as can be seen at Fig. I and Fig. II.

C. CONCLUSION

The aim of irradiation carried out with hides and skins in these experiments is to determine the optimum dosage of improving the physical and mechanical properties of leather raw materials.

It could be established that degradation and formation of three-dimensional structures always occur simultaneously when hides

and skins are irradiated with γ -rays.

Irradiation carried out with dosages between 0.1 to 0.3 Mrad results in the improvement of the tensile stretch.

In case of the tensile strength irradiation with a dosage about 0.5 Mrad gives better results than irradiation at other dose.

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