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THE EFFECT OF NUCLEAR RADIATION ON PLASTIC MATERIALS

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Plastics are organic materials. The carbon and hydrogen atoms in the plastic, bound together by covalent (electron pair) bonds, are easily broken by the addition of radiation energy <sup>1)</sup>.

The different types of atomic radiation can be conveniently subdivided into three categories:

- 1) charged particles;
- 2) uncharged particles, and
- 3) electromagnetic radiation.

The details of the modes of interaction of these various radiations differ, but the final effect is to produce ionization and molecular excitation in covalently bonded molecules <sup>1-6)</sup>.

The excitation and ionisation of a molecule usually lead to one or more of the following processes:

- breaking of chemical bonds leading to formation of free radicals <sup>\*)</sup>;
- rearrangement of the molecule;
- degradation of the molecule.

Once the physico-chemical processes are understood the change in physical properties can be predicted from a knowledge of the relationship between physical properties and chemical constitution.

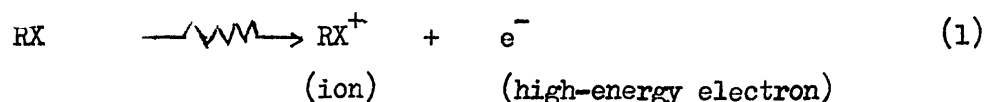
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\*) Highly reactive atom or group of atoms with one (or more) free electrons.

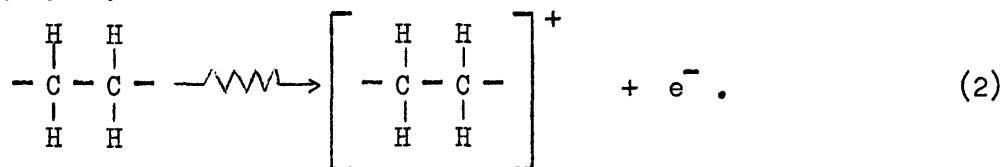
A. MECHANISMS 4-7)

1) Ionisation

When a high-energy charged particle passes close to a molecule of the absorbing material, the electrostatic field of the particle strongly influences the molecular electrons in their orbits. If the transfer of energy in this interaction is larger than the binding energy of an electron in its parent molecule, ionisation results.



e.g. polyethylene



The sign  $\text{---}\wedge\wedge\wedge\wedge\text{---}$  is conventionally used to denote the change following irradiation.

Such ionisation is proved by the observation of induced conductivity in many polymers under irradiation (see electrical properties page 12).

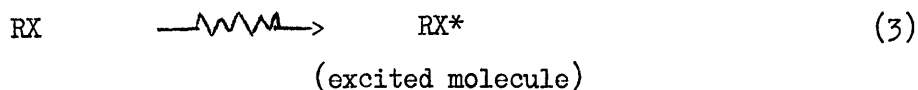
All electrons that are ejected from the molecules of the irradiated medium lose their kinetic energy by ionising and exciting in turn other molecules along or near their path, until their energy is down to thermal energy, after which recombination follows.

2) Excitation

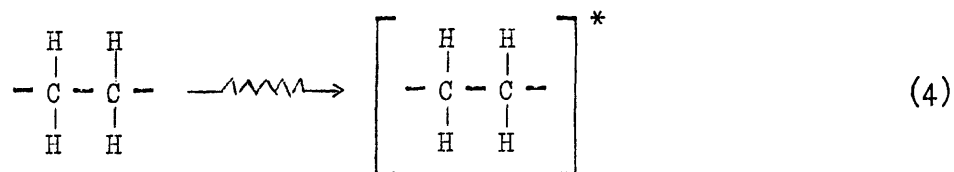
The excited molecules are produced by:

a) Direct excitation by fast moving particles

If the energy transferred to a molecular electron is below the lowest ionisation potential, it may still be large enough to displace the electron to an excited state.

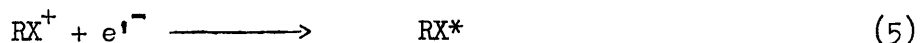


e.g. polyethylene

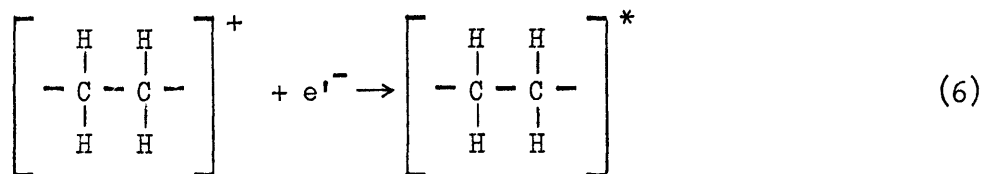


b) High excited states resulting from ion-electron recombination

The positive ion may capture a thermal electron ( $e'^{-}$ ).



e.g. polyethylene



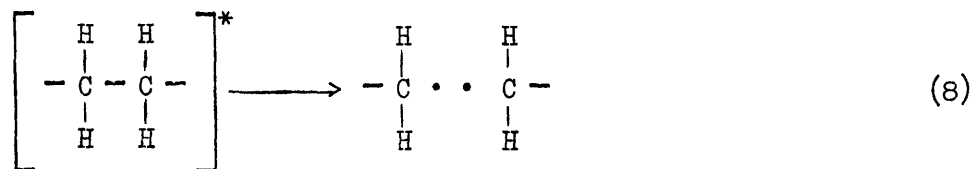
The energy gained by the molecule RX is equal to its ionisation potential; thus the molecule RX is placed in a high excited state, and the probability that it will undergo dissociation is very great.

3) Possible reactions involving excited molecules

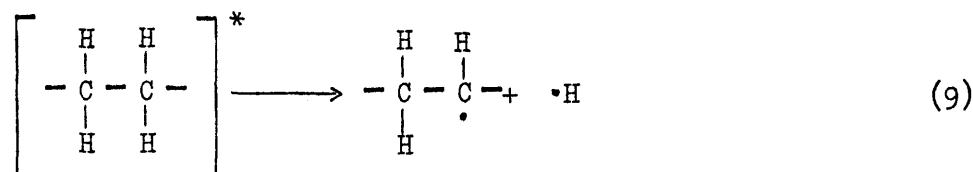
a) Dissociation into free radicals



e.g. polyethylene



or



This reaction is one of the most important sources of free radicals in radiation-chemical reactions. Since free radicals are chiefly responsible for the subsequent chemical changes, dissociation reactions of this type must be considered among the most important basic reactions.

The energy corresponding to the excited state is much larger than needed for breaking the chemical bond. This excess energy is carried off as kinetic energy by the radicals  $R\cdot$  and  $X\cdot$  (hot radicals) which can thus escape from the structure of the surrounding molecules and in such an event their recombination is less likely to occur.

b) Dissociation into molecular products

The excited molecule can also dissociate directly in neutral products:



where  $R_1$  and  $X_1$  are stable molecules.

4) Free radical reactions

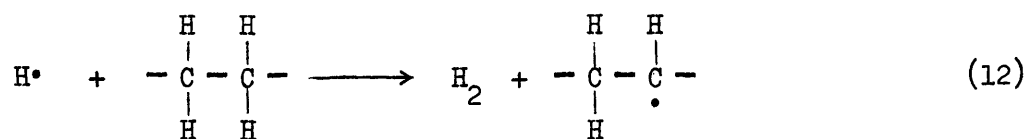
Some of the most important elementary free radical reactions are:

a) transfer reaction

A radical reacts with a molecule to abstract a hydrogen atom:



e.g.

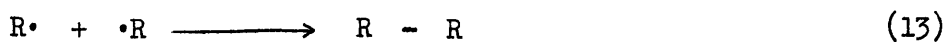


b) destruction reactions:

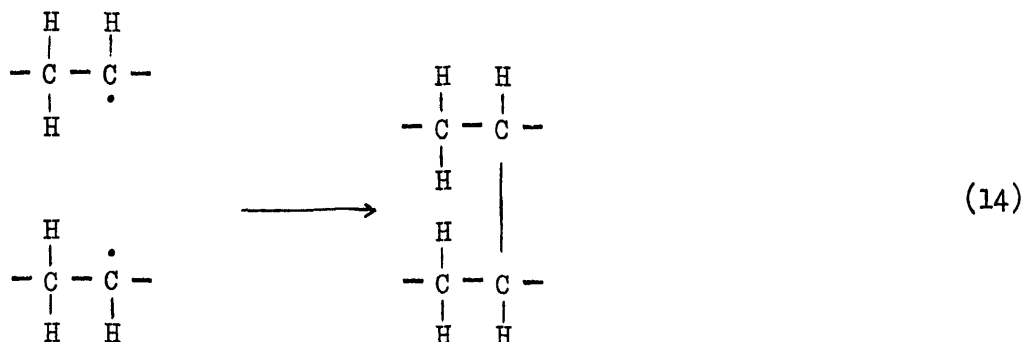
A free radical can only be destroyed in a given system by interaction with another radical. Such reactions can be of the following type:

- combination:

two radicals combine their unpaired electrons to form a chemical bond.

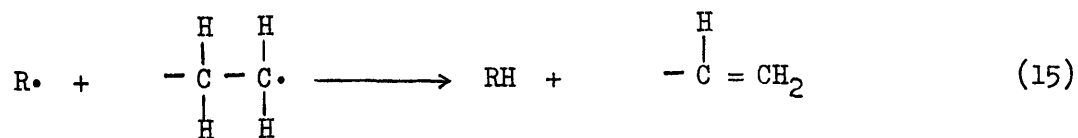


e.g.

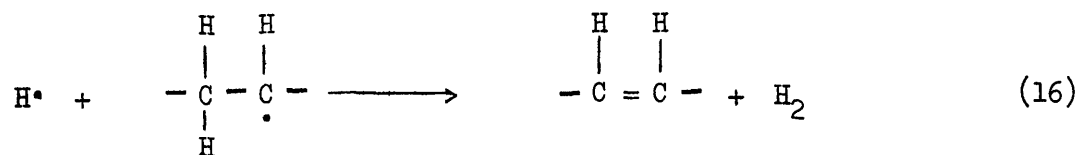


- disproportionation:

a hydrogen atom is displaced from one radical to the other leaving a double bond.



or



B. CHEMICAL CHANGES <sup>1,4-s)</sup>

All the processes studied above lead to one or more of the following effects in polymers:

a) crosslinking is the formation of chemical bonds between two polymeric chains according to the scheme:

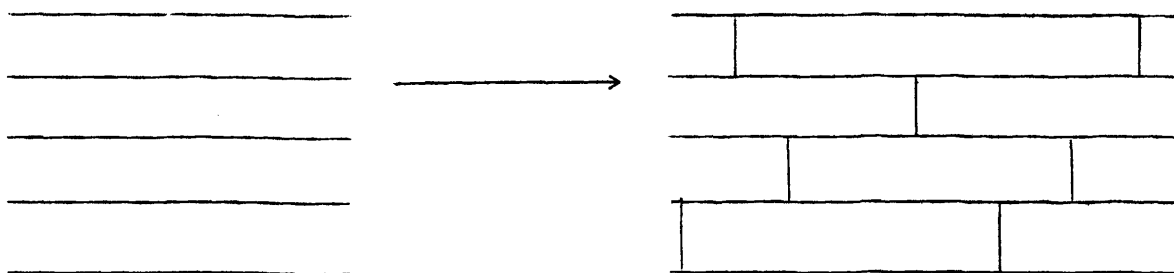


Fig. 1

This process results in increasing the molecular weight and eventually in the formation of a three-dimensional network.

A picture of a crosslinking reaction in a very simple polymer molecule is shown in Fig. 2. During irradiation, the reaction is started by the release of a hydrogen atom from the polymer chain, with the creation of a free radical. The hydrogen atom which has escaped abstracts another hydrogen atom from a nearby polymer and combines with it to form hydrogen gas. Then, the free radicals may combine with each other to form crosslinked molecules.

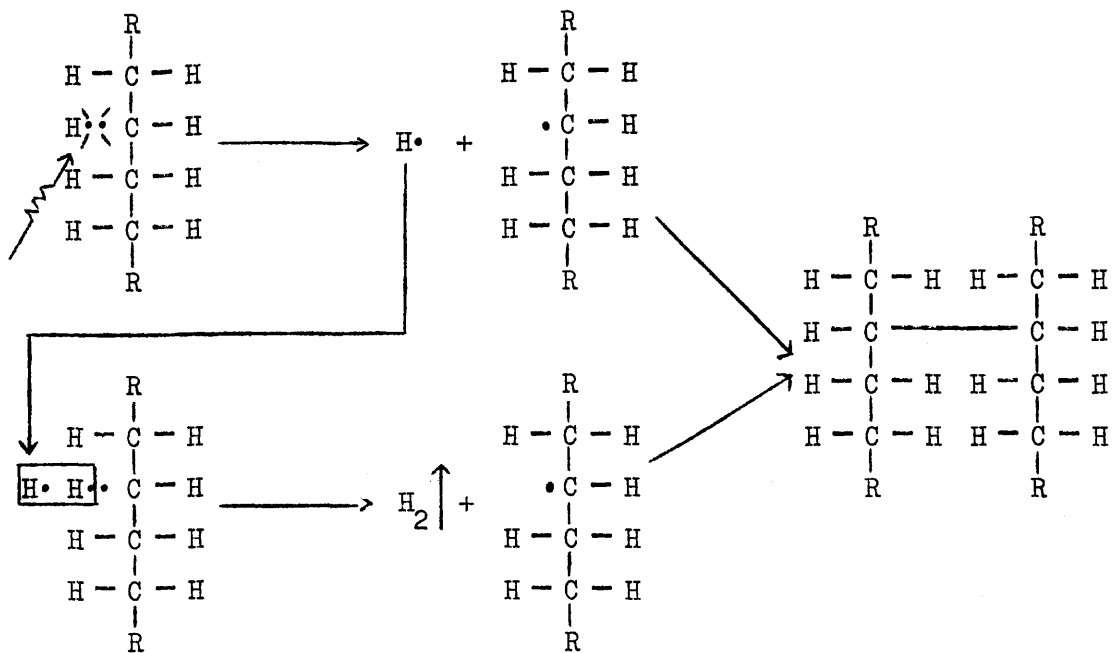


Fig. 2 - Illustration of crosslinking and gasformation

b) degradation is the fracturing of polymer molecules, leading to a decreased average molecular weight.

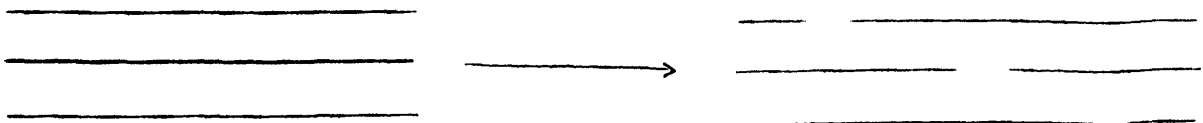


Fig. 3



The reaction starts with the fracture of the main chain into two smaller fragments. One of the fragments (free radicals) will react with a hydrogen atom forming a neutral molecule. The other fragment will become unsaturated through the release of a hydrogen atom.

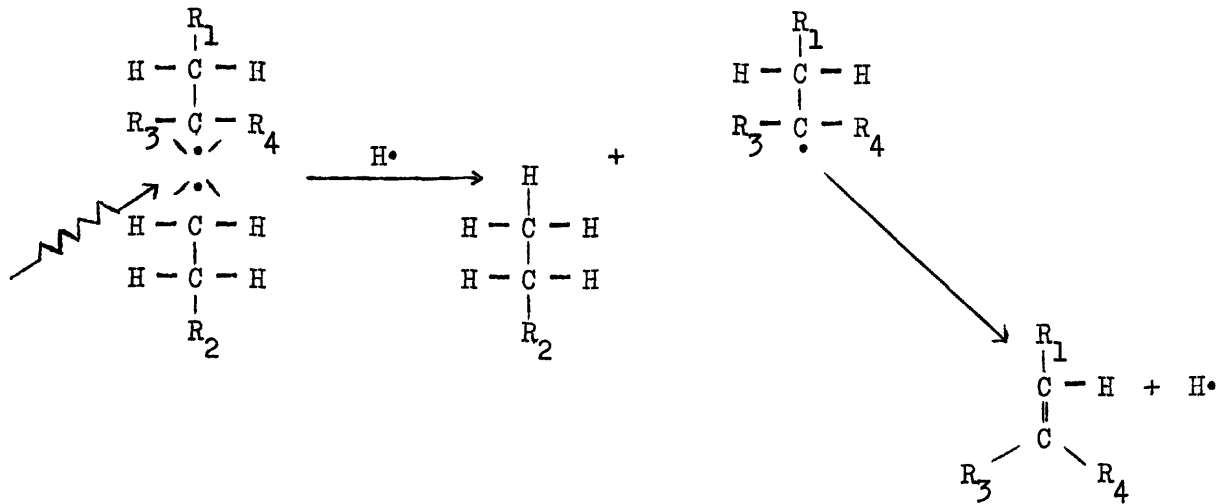


Fig. 4 - Illustration of cleavage and unsaturation

Materials which degrade tend to produce less gas than those which crosslink but in both processes a considerable amount of unsaturation occurs.

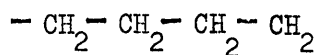
Even in those systems which initially crosslink, degradation will begin to predominate at sufficiently high doses.

The table shows the classification of polymers into the two indicated groups <sup>\*)</sup> 1):

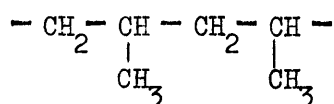
\*) A list of common trade names can be found in R. Sheldon, NIRL/R/58, (1963).

Polymers which crosslink

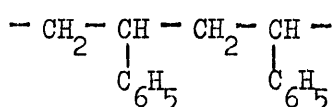
- 1) Polymethylene (polyethylene)



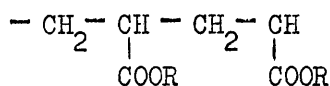
- 2) Polypropylene



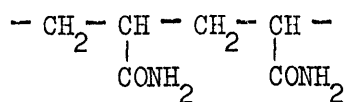
- 3) Polystyrene



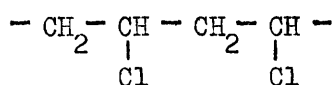
- 4) Polyacrylates



- 5) Polyacrylamide



- 6) Polyvinylchloride

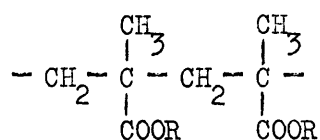


- 7) Polyamides

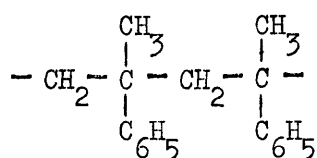
- 8) Polyesters

Polymers which degrade

- 1) Polymethacrylate



- 2) Poly-alpha-methylstyrene



- 3) Polytetrafluoroethylene

- 4) Polytrifluorochloroethylene

- 5) Cellulose and derivatives

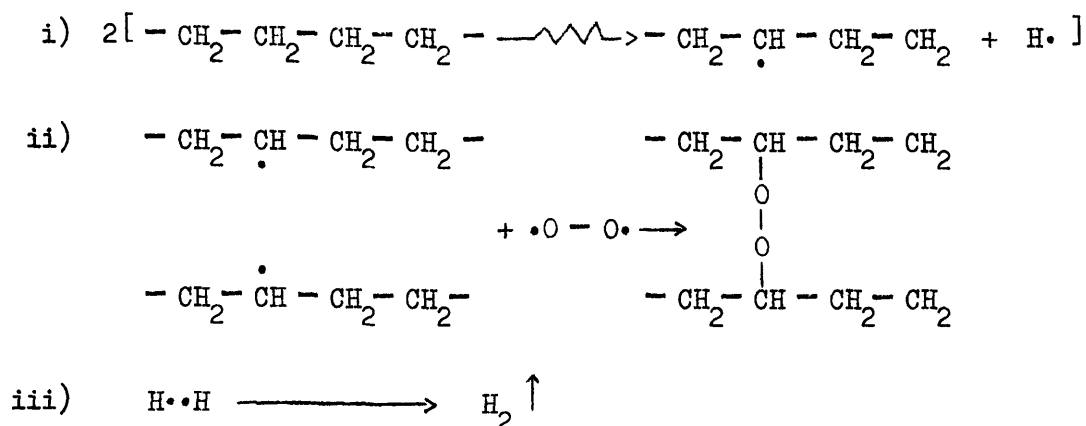
From the structure of the various polymers in the table it is seen that vinylpolymers in which two side chains are attached to a single carbon atom (e.g.  $-\text{CH}_2-\text{CR}_1\text{R}_2-$ ) degrade while those with a single side chain or no side chain (e.g.  $-\text{CH}_2-\text{CHR}_1-$  or  $-\text{CH}_2-\text{CH}_2-$ ) crosslink<sup>9</sup>).

While this rule is not universally valid, it does offer a useful approximation for the behaviour of polymers with a carbon backbone.

c) Influence of oxygen

The presence of oxygen during the irradiation is an important factor which may in some cases have a fundamental influence on the final issue of the radiolysis of solid polymers <sup>10)</sup>.

Since oxygen contains two unpaired electrons, this substance may act as a biradical, and in fact, it readily reacts with most organic materials : (e.g. polyethylene)



The resulting organic peroxides and hydroperoxides are relatively labile chemical structures, and a moderate amount of energy (radiation, heat, etc.) can split them.

The effects of oxygen show a marked dependence on dimensions of the sample and on the dose rate for many polymers. It has been shown that many, if not all, crosslinking polymers would probably undergo cleavage if irradiated in a highly divided form, i.e. with a large surface-to-volume ratio in the presence of large amounts of oxygen <sup>5)</sup>.

Polyethylene irradiated in air at high dose rates ( $10^8$  rad/hr) shows behaviour similar to that of polyethylene irradiated in vacuum. However, if the dose rate is low enough (380 rad/hr), the polymer is not completely cross-linked <sup>11, 12)</sup> even at high total doses. The reason for this seems to be that

the rate of diffusion of oxygen into the polymer is higher than the rate of consumption of radicals by the chemical reactions.

High energy radiations also have the ability to form ozone from oxygen. This can lead to reactions that are typical of ozone and which may have a destructive effect on the polymer<sup>13)</sup>.

### C. PHYSICAL CHANGES

#### 1) Mechanical properties

The influence of radiation on the mechanical properties of polymers differs widely depending on whether the polymers crosslink or degrade.

The crosslinking effect is characterized by:

- |                |                     |
|----------------|---------------------|
| an increase in | a) tensile strength |
|                | b) hardness         |
|                | c) softening point  |
| a decrease in  | d) solubility       |
|                | e) elongation       |
|                | f) elasticity.      |

A moderate amount of radiation may be beneficial to these materials but ultimately they lose practically all their mechanical properties.

Degradation always causes a steady decrease in most of the properties of polymers. They soften and become sticky or eventually disintegrate into a powdery substance.

When bulky pieces of plastics are irradiated, internal stresses can build up due to gas evolution, which may contribute significantly to the loss of mechanical properties. The internal stresses can be sufficient to develop cracks in the plastic and cause its final disintegration<sup>14)</sup>.

Extensive work was carried out by Sisman and Bopp<sup>15)</sup>, Charlesby<sup>1)</sup>, Collins and Calkins<sup>16)</sup>, Broadway<sup>17)</sup>, Marin<sup>18)</sup> and others.

2) Electrical properties - "Radiation induced conductivity" -

Ionisation and excitation effects in polymers have thus been shown to lead to the formation of more or less free electrons and free radicals. These manifest themselves in a variety of changes, both transient and permanent, in the physical and chemical properties of the organic material. As transient change can be given the enhancement of the electrical conductivity of polymers.

Polyethylene sheets <sup>19)</sup> were irradiated with 2 MeV X-rays at a dose-rate of several hundred rads per minute. The conductivity immediately increased to a factor of 1 000 after 20-40 sec of irradiation. This level remained constant throughout the period of irradiation. The total dose per sample was kept below 10 000 rads. At the end of the irradiation, the conductivity immediately dropped by a factor of 100 and then gradually returned towards its initial value. Similar changes are observed in other polymeric materials <sup>20, 21)</sup>.

The magnitude of the change of the electrical resistance is a function of the type of material that is being irradiated and the intensity of the irradiation <sup>1)</sup>.

In addition to the transient effect are the permanent changes (cross-linking and degradation) occurring in polymers subject to radiation. The electrical resistivity of all polymeric materials generally decreases with radiation. However, the decrease is small in comparison with their original resistivity, and electrical failure of organic insulators is usually due to mechanical deterioration rather than to gross changes in electrical properties <sup>15, 22)</sup>.

3) Colour changes

Some polymers show characteristic changes in colour produced by nuclear radiation. The colour changes depend on the conditions of irradiations such as vacuum, air, form of sample and temperature <sup>23, 24, 25)</sup>. The presence of trace amounts of additives (plasticizers, stabilizers, etc.) may further alter the discolouration <sup>1, 26)</sup>.

Most polymers turn yellow or brown under heavy irradiation, but the dose in which discolouration becomes noticeable varies widely depending on the chemical structure of the polymer. The changes in colour are no reference for indicating other physical effects (mechanical, electrical, etc.)<sup>15)</sup>.

Various interpretations have been proposed in order to account for the observed colour. It seems established that two major effects are responsible for discolouration, namely the formation of unsaturated bonds in the molecules<sup>27,28)</sup> and trapping of free radicals and ions<sup>23)</sup>.

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