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THE RADIATION DEGRADATION OF POLYPROPYLENE

*Its present status, and the stabilisation of
polypropylene against ionising radiation*

by

G. de Hollain



ATOMIC ENERGY BOARD
Pelindaba
PRETORIA
Republic of South Africa

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PELINDABA
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ISBN 0 86060 640 2

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SAMEVATTING

Weens polipropileen se voortreflike eienskappe word dit op groot skaal vir die vervaardiging van wegdoenbare mediese artikels gebruik. Ongelukkig leen hierdie polimeer sig nie juis goed tot stralingsterilisering nie omdat die gehalte tydens bestraling aansienlik verswak wat die meganiese eienskappe van die polimeer beïnvloed. In hierdie verslag word die uitwerking van straling op polipropileen bespreek vir sover dit die veranderinge betref wat in sy meganiese en fisiese eienskappe veroorsaak word. 'n Navorsingsprogram word voorgestel om die stralingsdegradering van hierdie polimeer tot die minimum te beperk deur die toevoeging van kruisbindingsmiddels om die nadelige uitwerking teen te werk. Daar word voorts ook voorgestel dat 'n proses van polimeeruitgloeing ondersoek word om die degradering van die polipropileen na bestraling sover moontlik te verminder.

ABSTRACT

Polypropylene is used extensively in the manufacture of disposable medical devices because of its superior properties. Unfortunately this polymer does not lend itself well to radiation sterilization, undergoing serious degradation which affects the mechanical properties of the polymer. In this paper the effects of radiation on the mechanical and physical properties of polypropylene are discussed. A programme of research to minimize the radiation degradation of this polymer through the addition of crosslinking agents to counteract the radiation degradation is proposed. It is furthermore proposed that a process of annealing of the irradiated polymer be investigated in order to minimize the post-irradiation degradation of the polypropylene.

1. INTRODUCTION

The production of polypropylene increased steadily from its commercialisation in 1958 until, in 1970, it reached 20 % of the output of polyethylene, the most widely used polymer at present [1]. Polypropylene is used for numerous purposes, for example for the manufacture of disposable medical items. At present about eighty per cent of the disposable syringes used in South Africa are made of polypropylene [2].

The change in hospitalisation practice brought about by the introduction of disposable medical devices (used only once and then discarded) resulted in an increase in demand for a large variety of sterile disposable medical products. At about the same time radiation sterilisation was introduced as an industrial sterilisation technique, providing the required capacity for the sterilisation of large volumes of disposable medical items. Whether cobalt-60 or electron accelerators are used in this technique, it enjoys indisputable advantages over classical processes [3,4].

Unfortunately, as compared with the polyethylenes, polystyrene and phenol resins, polypropylene offers little resistance to irradiation; its brittleness increases rapidly with an increase in radiation dose. Tensile strength and impact strength are the two mechanical properties which determine the brittleness of the polymer and its usefulness as a radiation-resistant material [5,6].

The object of this report is to propose a study for the stabilisation of polypropylene against ionising radiation as a means of compounding a polymer suitable for radiation sterilisation. We shall approach the problem from three different angles, viz. the effect of the dose rate, which can limit degradation [7], the effect of additives in the polymer during irradiation [8], and the phenomena occurring during the post-irradiation period [9].

The effects of gamma rays on the properties of the polypropylene will be determined by the changes in the molecular mass, the variation of the ratio between degradation and crosslinking, the development of the gel content, and the modification in the mechanical properties.

2. RADIATION DEGRADATION

2.1 Polymer Structure

Polypropylene is a poly- α -olefin with three conformations, viz. an isotactic, syndiotactic and atactic polymer (Fig. 1).

Polymerisation of propylene can be stereospecific, depending on the Ziegler-Natta catalyst used [10]. The organometallic catalysts of Ziegler and Natta operate in a heterogeneous medium and cause the molecular masses to have a wide distribution; the ratio of the weight-average molecular mass to the number-average molecular mass, M_w/M_n varies between 2 and 10, fixed for each catalytic system [11,16].

The isotactic variety of the polypropylene isomers is the one of major commercial interest. The polymer has a degree of crystallinity of between 50 % and 80 %. Whatever quenching process is used, it crystallises very easily and an equilibrium value of 80 % is reached after about one year [12].

2.2 Chemical Mechanisms of Radiation Degradation

2.2.1 GAS EVOLUTION AND UNSATURATION

Hydrogen and methane represent 99,5 % of the gases formed during the irradiation of polypropylene, methane being only 2,5 % of this percentage [13].

The infrared spectrum of irradiated polypropylene reveals an increase in vinylidene unsaturation [14]. The unsaturation is related to the evolution of hydrogen and the rupture of the main chain in accordance with a disproportionation mechanism [15], viz.:

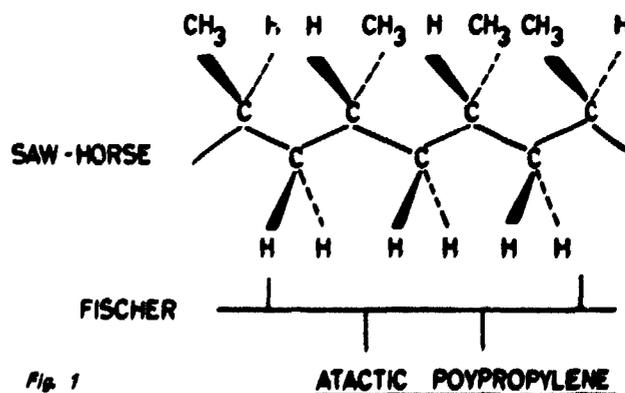
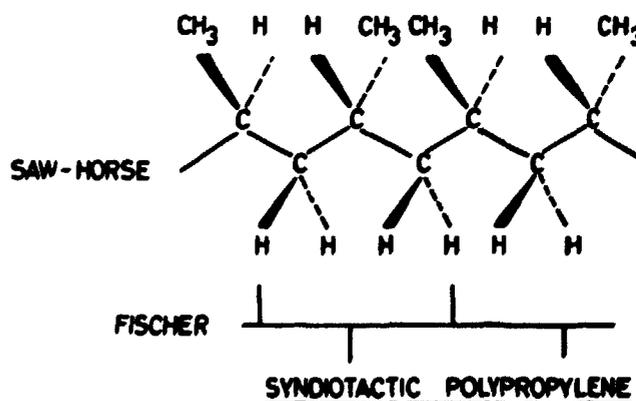
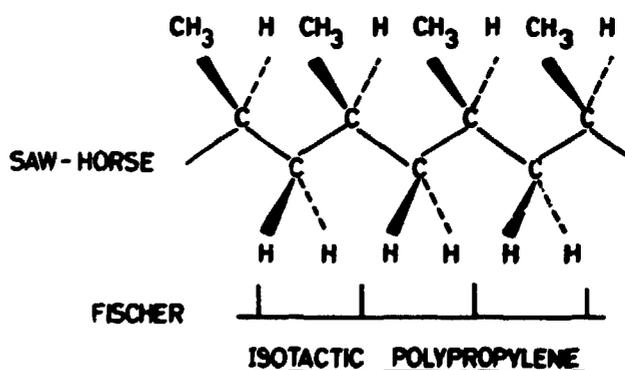
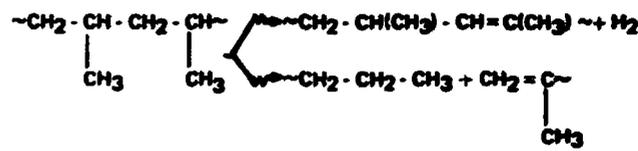
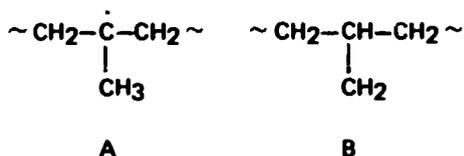


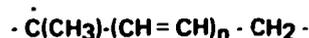
Fig. 1

2.2.2. FORMATION OF RADICALS DURING IRRADIATION

Two types of ESR spectra are obtained from irradiated polypropylene. In the first instance, two radicals can be detected, viz.:



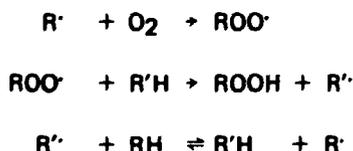
Since radical B is stable only at low temperatures, it is transformed into radical A at ambient temperature [17]. The second type of spectrum indicates the existence of polyenyle radicals, i.e.,



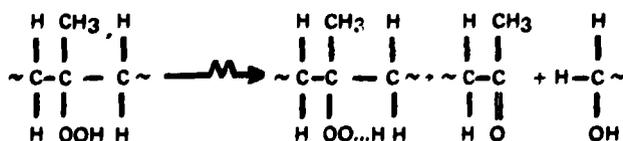
which are stable at ambient temperature ($n = 1$ or 2). Longer conjugated chains are observed when the dose reaches values of thousands of kGy [18].

2.2.3 DEGRADATION IN THE PRESENCE OF OXYGEN

From -140°C upwards oxygen reacts with the radiation-formed radicals to form peroxy radicals. These radicals abstract a hydrogen atom from a neutral molecule and are transformed into hydroperoxides [19]. At the same time they give rise to new radicals. At ambient temperature this chain-reaction mechanism comprises the following [20]:



The hydroperoxide and carbonyl groups characterise the degree of oxidation of the polypropylene, and their absorption can be measured by infrared spectroscopy [21]. Veselovskii *et al* [22] proposed a possible decomposition mechanism of the hydroperoxide groups to explain the rapid decrease in molecular mass, viz.:



(intrinsic viscosity method) during the irradiation of isotactic polypropylene. The decomposition of hydroperoxide groups linked with secondary carbon atoms does not cause a chain rupture. This phenomenon partly explains the higher stability of polyethylene [23].

Carlsson *et al* [21] showed by preferential oxidation of films that the photostabilisation of polypropylene depends on the diffusion of oxygen into the matrix.

The mechanisms of thermal decomposition [24] and photolysis [25] are similar to those just described. Tsuchiya *et al* [26] studied the products of thermal degradation of polypropylene in the absence of oxygen. They explain the distribution of the products by a process of intramolecular radical transfer.

2.2.4. CROSSLINKING AND CHAIN SCISSION

The main characteristics of the effects of ionising radiation on linear polymers are their ability to undergo crosslinking or degradation, depending on their structure. A general empirical rule applies to this phenomenon. If each carbon atom of the chain carries at least one hydrogen atom, the polymer is crosslinked, whereas the polymer is degraded if one tetrasubstituted carbon atom is present in the monomer unit [27]. The β/α -ratio can be measured for each polymer α and β respectively representing the probabilities of crosslinking and scission. Since the formation of a crosslink requires two polymer units, the equivalence is defined as follows:

$$\beta/\alpha = \frac{G \text{ scission (S)}}{2G \text{ crosslinks (X)}}$$

where G represents the number of molecules transformed by the absorption of 100 eV [28]. The G value was extended to include the number of chemical events produced by the absorption of 100 eV, viz. G(C=C) number of carbon double bonds, G(R \cdot) number of free radicals formed, and G(-M) number of monomer molecules disappearing.

The β/α -ratio fluctuates between 0,8 and 1,0 with G(X) \cong 0,6 and G(S) \cong 1,1 [29] for isotactic polypropylene at ambient temperature. The β/α -ratio of polyethylene is no more than 0,15, which explains its higher radiation resistance.

When the dose is increased and the density of crosslinking reaches one crosslinked unit per molecule, the critical conditions have been reached for the formation of an insoluble three-dimensional network called a gel [27].

By comparing the dose and the gel fraction, Charlesby and Pinner [30] obtained a linear relation between $s + s^{1/2}$, where s represents the soluble fraction and the inverse of the number of crosslinks, or the inverse of the radiation dose. This equation can be written in the following form:

$$s + s^{1/2} = \frac{1}{2} \lambda + \frac{100 N_A}{M_{w,0} G(X) r}$$

where s represents the fraction in weight of the soluble component after dose r (in eV/g), λ the G(S)/G(X) ratio, N_A the Avogadro number and $M_{w,0}$ the initial weight-average molecular mass. For a dose expressed in kGy, the equation is as follows:

$$s + s^{1/2} = \frac{1}{2} \lambda + \frac{9,85 \times 10^6}{M_{w,0} G(X) r}$$

This equation can be converted in terms of dimensionless quantities [31] to

$$s + s^{1/2} = \frac{1}{2} \lambda + (2 - \frac{1}{2} \lambda) (r_g/r)$$

where r_g is the dose at gel point. At infinite dose we have

$$s + s^{1/2} = \frac{1}{2} \lambda$$

The accuracy of the last-mentioned linear extrapolation was contested by the theories of Inokuti and Saito who studied gel formation as a function of the initial molecular mass distribution. Inokuti [32] applied the generalised Poisson distribution (henceforth called the Schulz-Zimm distribution) to the Charlesby equation. The initial distribution $m(P,0)$ is expressed as follows for $\beta > 0$:

$$m(P,0) = \frac{\beta^{\beta+1}}{P_{n,0}^2 \Gamma(\beta+1)} \left(\frac{P}{P_{n,0}}\right)^{\beta-1} \exp\left(-\frac{\beta P}{P_{n,0}}\right)$$

where $m(P,0)$ is the number of polymer molecules at dose 0 with a degree of polymerisation P , Γ is the gamma function, and β the width of distribution. Parameter β is inversely proportional to the dispersivity as follows:

$$\beta = \left(\frac{\bar{M}_w}{\bar{M}_n} - 1\right)^{-1}$$

The curves obtained by Inokuti reveal an overestimation of λ for a wide initial distribution ($\beta < 1$), and an underestimation of λ for a narrow initial distribution ($\beta > 1$). By using the experimental values determined by Schnabel and Dole for polypropylene [33], Inokuti and Dole [34] found that the calculated curve and the experimental curve agree quite well. Since the preceding theory cannot be applied to polyethylene, Saito *et al* [31] resumed Inokuti's calculation by using the Wesslau distribution of which the form is as follows:

$$m(P,0) = \frac{1}{\beta \sqrt{\pi P^2}} \exp\left(-\frac{1}{\beta^2} \left(\ln \frac{P}{P_{n,0}}\right)^2\right)$$

where

$$\beta = \sqrt{2 \ln \frac{\bar{M}_w}{\bar{M}_n}}$$

Saito *et al* found that the calculated curves and the information published by several authors agree quite well. They show that the slope at the gel point of $(s + s^{1/2})$ plotted against (r_g/r) is more helpful in many cases in determining the value λ than the intercept at infinite dose.

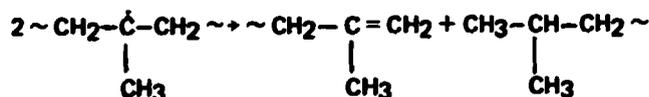
In the case of irradiated polypropylene, several authors [33,35,36] could not obtain a straight line in the non-normalised Charlesby-Pinner function $(s + s^{1/2})$ plotted against $1/r$. In fact, the molecular mass distribution of this polymer is far removed from the most probable one. Charlesby and Pinner used this hypothesis of $\bar{M}_w = 2 \bar{M}_n$ for their equation. These facts result in the hypothesis that chain scission causes randomisation of the initial molecular mass distribution, so much so that the system can be treated as having a most-probable distribution. Recent studies [37,38] have corroborated these facts and have

demonstrated that the dispersivity of polymethyl methacrylate (PMMA) and polystyrene in solution reached a constant value of close to 2 after a determined dose corresponding with a number of scissions.

2.2.5 POST-IRRADIATION EFFECTS

In irradiated polypropylene, certain free radicals are relatively stable at ambient temperature. They can produce crosslinks and/or oxidative scissions. Sobue and Tazima [39] managed to increase the gel content significantly after irradiation by heating a sample under vacuum at a temperature close to fusion.

Among the numerous reactions which can be responsible for the disappearance of free radicals in the absence of oxygen [40], only the process of disproportionation can result in a decrease in molecular mass.



Though small, this decrease was observed when irradiated polypropylene was stored under vacuum in the absence of oxygen [41]. Waterman and Dole [42] indicated the limited role of disproportionation by concentrating on the small increase of the vinylene groups when reheating the irradiated polyethylene.

The marked effect of oxygen on the decrease in molecular mass of polypropylene during and after irradiation can be seen in Fig. 2.

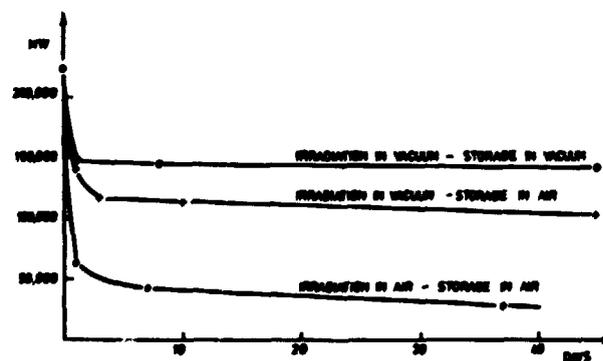


Fig. 2 EFFECT OF STORAGE CONDITIONS ON IRRADIATED POLYPROPYLENE

Main chain scission can result from the disproportionation of a hydroperoxide radical to form a hydroxide and a ketone group [43]. This mechanism has, however, not as yet been completely explained [44].

2.3 Effect of Dose and Dose Rate

2.3.1 DOSE

The relations which link the elasticity modulus of a polymer with the crosslinking density [7] thereof, reveal the gel content to be the criterium of improvement of the mechanical properties. A dose of about 500 kGy (50 Mrad) is needed in the case of polypropylene to obtain an insoluble gel fraction [14]. Since an average dose of 25 kGy (2.5 Mrad) is required for purposes of radiation sterilisation

[4], this polymer must be treated in such a manner that a gel fraction can form at a low dose to counteract the adverse mechanical effects resulting from chain rupture. If gel formation cannot be achieved, the presence of an additive is justified to retard the radiation degradation.

2.3.2 DOSE RATE

The constant development of the technology of electron accelerators has ensured dose rates which can reach values of several hundreds of kGy (tens of Mrad) per second. The question can be put whether the creation of high local concentrations of radicals would favour their recombination. In fact, this reaction can be competitive in relation to those which are limited by the diffusion of oxygen into the polymer. At any rate, it must be remembered that the radicals can migrate by successive hydrogen abstractions [22], even in a molecule [40]. As far as the recombination of radicals is concerned, the discovery of radical pairs has revived interest in the irradiation of organic solids [45]. The intrinsic value of formation of these radical pairs implies that they are not due to an occasional overlapping of the spurs. Quite unexpectedly, Iwasaki *et al* [45] established that the ratio between the radical pairs and the isolated radicals decreased with an increase in dose.

2.4 Changes in Mechanical Properties

The rheology of polymers can be studied on the basis of their viscoelastic properties and the limiting behaviour of the material after it has been exposed to various stresses. The creep function represents the variation of strain as a function of time under the effect of a constant load. This function has the dimensions of a compliance, i.e. the inverse of a modulus. Creep measurements made on polypropylene [46] have proved allyl methacrylate monomer to be an effective crosslinking agent. These experiments were conducted at 180 °C in order to eliminate the effect of crystallinity. The relaxation function which describes the stress variation for a constant strain, possesses the dimensions of a modulus. This type of investigation is applied in particular to elastomers whose predominant quality is strain reversibility [47].

The following are a few of the mechanical properties which can be tested by standard methods, viz. tensile strength, elongation, impact strength, tear strength, stiffness in flexure, water permeability and temperature resistance. The principal properties of polypropylene are listed in Table I [48], in comparison with its competitors.

TABLE I
MECHANICAL PROPERTIES OF PLASTIC MATERIAL

	TENSILE STRENGTH ASTM D - 638 (kg/cm ²)	PERCENTAGE ELONGATION AT YIELD ASTM D - 638 (kg/cm ²)	FLEXURAL STRENGTH ASTM D - 790 (kg/cm ²)	IZOD IMPACT STRENGTH ASTM D - 256 (ft lb/in. of notch)
CTFE	316 - 422	80 - 230	654	2,6
POLYCARBONATE	562 - 668	100 - 130	679	12 - 18
POLYETHYLENE LD	42 - 162	90 - 800		
POLYETHYLENE MD	84 - 246	50 - 600	337 - 492	0,5 - 15
POLYETHYLENE HD	218 - 387	30 - 1000		0,5 - 20
POLYPROPYLENE	302 - 387	200 - 700	422 - 562	0,5 - 2
POLYSTYRENE	352 - 844	1 - 2,5	633 - 984	0,3
POLY (VINYL CHLORIDE)	352 - 633	100 - 1000	703 - 1126	0,4 - 20
PVC/PP	352 - 662	100 - 140	773 - 1055	0,4 - 32
POLY (VINYLIDENE CHLORIDE)	211 - 352	10 - 250	281 - 422	1

Polypropylene possesses more rigidity and greater tensile strength than high-density polyethylene. Its stress-cracking resistance is very high and its impact strength acceptable. In comparison with polyethylene, the polypropylene homopolymer has a better temperature resistance but turns brittle at low temperature (5 °C) [47]. Polypropylene bears up well under the attack of a very large variety of chemical substances [49]. One of its most spectacular properties is its high resistance to dynamic fatigue tests, which has made it a popular integral hinge. Polypropylene also enjoys the advantage that a crack which is due to tension in the material propagates more slowly than in polyethylene [50].

Most of the details in respect of the limiting properties of a thermoplastic are based on stress-strain curves and impact-strength tests. These mechanical properties are modified by radiation. The stress-strain curves determine the elasticity modulus or Young's modulus, the elongation

and tensile strength at yield, the elongation at break, the ultimate tensile strength and the drawing stress [51,47]. The general shape of a stress-strain curve for a thermoplastic material is shown in Fig. 3.

Elasticity-modulus measurements were widely used to estimate crosslinking above fusion temperatures and/or vitreous transition temperatures [20], especially in the case of elastomers [52].

With regard to commercial polypropylene samples, Dasgupta [5] recorded an average gain in limit tensile strength of 17 and 21,5 % for doses of 25 and 50 kGy (2,5 and 5 Mrad) respectively. These values drop by about 5 % during a storage period of 18 months. They agree with those obtained by Benderley and Bernstein [46], who observed that the tensile strength of polypropylene increases up to 50 kGy (5 Mrad) and then decreases rapidly with an increase in radiation dose.

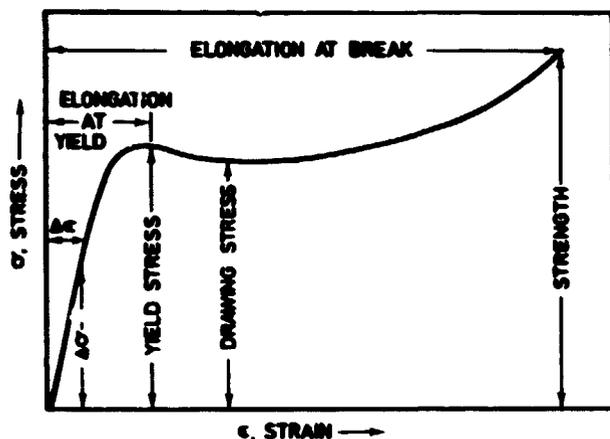


Fig. 3 GENERAL FORM OF STRESS-STRAIN CURVE FOR A PLASTIC MATERIAL

The impact strength of polypropylene is very adversely affected by radiation. In comparison with high-density polyethylene, the impact strength increases with a decrease in degree of crystallinity. The degree of crystallinity tends to be associated with a high molecular mass [50]. Note, in passing, that the impact strength of polypropylene depends largely on the orientation given during processing. The strength is higher along the flow direction than in the cross-flow direction [53]. It was noted that polypropylene is notch-sensitive [48], after most of the impact-strength tests had been done on notched samples. Consequently, the reproducibility of the results depends on the quality of the notch, and special precautions must be taken in the design of articles to be made from this polymer. Finally, we cannot disregard the experiments conducted by Sakaguchi *et al* [54], who observed the scission of the main chain and the appearance of radicals when a mechanical fracture was made in bulk polypropylene.

2.5 Role of Additives

2.5.1 GENERAL SCHEME

The preponderant role played by additives is of a twofold nature. They enable the reaction mechanisms resulting from the ionising radiation to be explained, but they are also able to modify the ultimate behaviour of the excited species which result from the interaction between radiation and the polymer.

In view of the actual state of knowledge, ionic processes cannot be dissociated from those which are based on excited molecules. This statement is even more justified when additives such as N_2O [55] and CCl_4 [56] are used, which are known to scavenge an electron by dissociative attachment and to undergo electronic-excitation transfer. We therefore compare the effect of an additive with a time scale which corresponds with the dissipation of energy in the medium.

The photons of cobalt-60 act upon the atoms of the irradiated material by the Compton effect. The ejected electrons release their energy during ionisation (secondary ions and electrons) and excitation. This initial stage is called

the physical stage and lasts for 10^{-15} s. During the physicochemical stage of between 10^{-15} and 10^{-12} s, the primary species are transformed on the site where they are formed. These processes of fragmentation, neutralisation and isomerisation yield radicals and stable molecular products. Finally, during the chemical stage the active species with a long lifetime react with one another or with the molecules of the matrix to yield the final products. These ions and radicals can migrate in the matrix. The last stage occurs during a delay of 10^{-12} s after the primary process and can last several hours, even several months, after irradiation.

The additives intervene on different levels in the above events and their presence during irradiation modifies the energy distribution before the actual chemical stage. For this reason we consider it judicious to introduce a model which represents the transfer of energy and which can be used for the ultimate selection of an additive.

2.5.2 MOLECULAR-EXCITON MODEL

By applying the molecular-exciton model to alkane polymers, Partridge [57,58,59] obtained an energy distribution whereby a large number of primary phenomena can be predicted. The molecular exciton is defined as resonance interaction between weakly coupled aggregate systems [60]. This non-ionised excited system is made possible by the regularity of the network of a molecular crystal. The main characteristic of this model is that the excitation energy is divided into two distinct parts, viz. one part situated inside C-H bond pairs connected to one common carbon atom, and the other which can migrate from one bond to the next along the main chain [57]. These excitons have a lifetime of between 3×10^{-13} and 10^{-14} s [61] and an average energy of 8.5 eV. Migratory excitons have a G value of < 3.8 . This theory accounts for the ratio of C-H to C-C bond scissions for polyethylene, the production of hydrogen, unsaturation and the production of radicals.

Nevertheless, with regard to the scission of the main chain in branched polymers, the exciton model appears to fail completely. The high G(S) value of 0.67 of polypropylene cannot be explained. Partridge attributes this discordance to dissociative ionisation [59]. Okada [55] shows that in the case of polyethylene, crosslinking and unsaturation are enhanced by N_2O and Xe. Since the mode of excitation of the main chain does not depend on that of the C-H bonds, Partridge [59] explains the phenomenon by attributing to Xe the possibility of absorbing the excitation energy of the C-C bonds and restoring it to the C-H system. He established agreement between the absorption bands of the additive and the energy levels of the C-C bonds which range from 8.5 to 10 eV.

2.5.3 INHIBITORS AND PROMOTORS OF CROSSLINKING

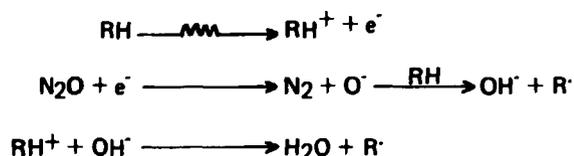
Apart from oxygen, whose effect has been described earlier, the main additives which inhibit crosslinking are iodine, methanethiol, isopropyl alcohol and isopropylamine, hydrocarbons such as isobutane, certain ketones, the phenols and the pyrocatechol derivatives [62]. These products can either react with the radicals to produce other less reactive radicals, or they can undergo hydrogen

abstraction. In the case of methyl-3 pentane, for example, the tertiary hydrogen is easily abstracted by a polymeric radical. The new radical will recombine later without contributing towards crosslinking [9].

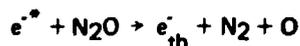
The compounds which favour crosslinking include some of the polyfunctional monomers [41,63,64], the electron scavengers [8], ammonia [9], and acetylene [41,65].

Odian and Bernstein [66] obtained a 70 % gel at 50 kGy (5 Mrad) by swelling at equilibrium (5.5 %) samples of polypropylene with allyl acrylate and allyl methacrylate. At this dose the untreated polypropylene yields no gel. These investigations were complemented by those of Charlesby and Fydeler [67], who demonstrated the efficiency of acrylic and methacrylic acids as crosslinking agents. The experiments with polyisobutylene, which crosslinks in the presence of allyl acrylate [66] and of N_2O [55] reveal the necessity of taking into account processes of energy transfer, since in the absence of these compounds polyisobutylene merely degrades.

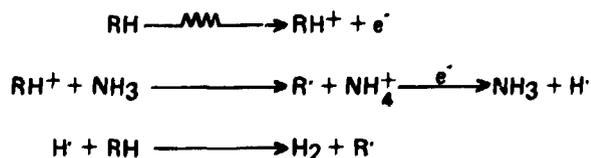
The part played by electron scavengers as crosslinking agents [8] seems to be based on the dissociative attachment which they undergo in accordance with the following reaction mechanism:



This category includes chlorobenzene, carbon disulphide, neopentyl chloride, sulphuryl chloride, thionyl chloride and sulfur hexafluoride. All of these additives have a favourable effect on the crosslinking of ethylene-propylene copolymer. The effect of N_2O on the crosslinking of polypropylene [36] has as yet not been quite clarified, and an attempt was made in a recent study [68] to prove that N_2O contributes toward the thermalisation of the electron:



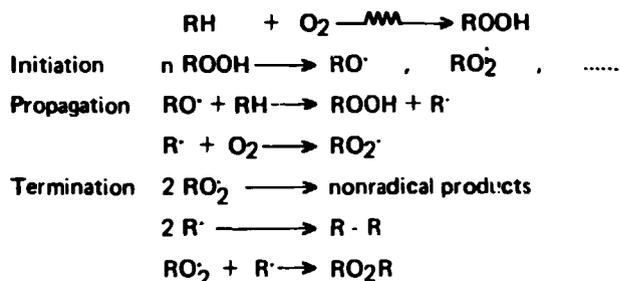
The mechanism in respect of the effect of ammonia [9] is based on the capture of the positive charge by NH_3 :



The mechanisms which are put forward to explain the behaviour of acetylene [69] are of a speculative nature and need to be studied more thoroughly.

2.5.4 RADICAL SCAVENGERS AND ANTIOXIDANTS

This category of additives is used to protect the polymer against the oxidative chain degradation. It can be initiated by heat or radiation, and is usually self-maintaining in accordance with the following reaction scheme [70]:



The stabilisation process consists of interrupting the above scheme by adding a compound which will react with R^\cdot or RO_2^\cdot to produce less reactive radicals or stable products [71]. The main antioxidants used for polypropylene, which are relatively radiation-resistant, are 2,6-di-*t*-butylmethylphenol, the bisphenols and 3,5-di-*t*-butylpyrocatechol. Pyrocatechol- α -naphthol cyclic phosphate and 2,6-di-*t*-butyl-4 methyl-phenyl cyclic phosphite preserve their antioxidising properties well in irradiated polypropylene [72].

3. STABILISATION OF POLYPROPYLENE

3.1 Thermal Stabilisation

Thermal degradation of polypropylene was studied in the presence [25,73] and absence of oxygen [27]. In this polyolefin the degradation is caused not by depolymerisation (loss of monomer) but by random scission of the chains. This process will therefore not be affected by an additive, and only a crosslinked polymer will have better thermal resistance. The degradation thus depends strongly on the number of bonds and their dissociation energies.

Once oxidation has been initiated, it propagates through the noncrystalline region of the polymer [74], and the chain reaction must be interrupted to decrease degradation. Stabilisation consists in preventing the decrease in molecular mass caused by the fragmentation of the peroxy radicals. The antioxidants should also possess appropriate thermal resistance for processing polypropylene.

3.2 Stabilisation Against Photodegradation

Most of the polymers are sensitive to the wavelength region of solar energy ranging from 300 to 400 nm. The higher energies are absorbed by the ozone layers of the atmosphere and do not reach us. The energies of the C-Cl, C-O and C-C bonds are situated in the aforementioned region. The photodegradation of the polyolefins is attributed to the carbonyl group. This chromophore is one of those which absorb predominantly in the proximity of the ultraviolet region.

During the production of polypropylene, the hydroperoxides give rise to two types of macroketones which undergo photolysis through the mechanism [75] shown in Fig. 4.

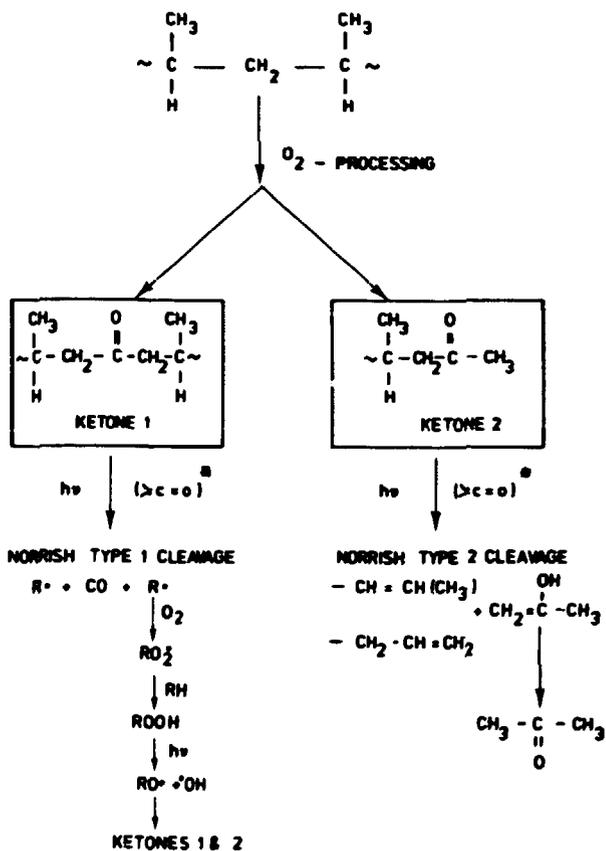


Fig. 4

PHOTODEGRADATION OF POLYPROPYLENE

Three possibilities exist whereby photochemical reactions can be inhibited from initiating degradation, viz.:

1. use of an ultraviolet screen, to prevent light from penetrating the polymer;
2. preferential absorption of the ultraviolet rays by a compound which dissipates the energy;
3. addition of a compound which is able to absorb the energy of the excited state of the polymer (this mechanism is called quenching).

In the first category, suitably dispersed carbon black is the most effective ultraviolet screen. The second category comprises ultraviolet absorbers of which the most widely used are the derivatives of salicylic esters, substituted benzotriazoles and orthohydroxy-benzophenones [76]. The last category of stabilisers contains chromium and nickel chelates [77,78]. The monohydroxy-benzophenones and the substituted hydroxyphenylbenzotriazoles are recommended as absorbants to stabilise polypropylene photochemically [79]. Contrary to polyethylene, a certain synergism* between the effect of the antioxidant and the effect of the UV absorbant is found in the above polymer.

*Synergism: Effect (a + B) > Effect A + Effect B

3.3 Protection Against Ionising Radiation

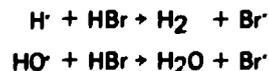
Polypropylene is, as a result of its branched structure, very sensitive towards ionising radiation. Apart from the ruptures of the main chain ($G(S) = 1.1$), the high initial concentration of radicals must be mentioned. At 77 K, $G(R\cdot) = 6.2$ for polypropylene [80], whereas this value is only $G(R\cdot) = 3.3$ for polyethylene [81]. Post-irradiation oxidation occurs more rapidly when the relative lifetime of the radicals of polypropylene is longer at ambient temperature.

Three means are available for protecting a polymer against ionising radiation, viz. the addition of an additive which can result in the transfer of energy away from the polymeric chain, the use of a scavenger to react with the active species (ions or radicals) which are responsible for the degradation, or a decrease in the $G(S)/G(X)$ ratio.

In the case of polypropylene, no specific protective agent exists. Many antioxidants have a protective effect against radiation in view of their strong aromatic structure [62]. Several authors have studied the relative stability of these compounds, but the behaviour of an antioxidant when exposed to radiation is too complicated and of little importance in the stabilisation of polypropylene. Recent research has concentrated on additives which cause gel formation at relatively low doses [41]. As we saw earlier, certain monomers and acetylene are effective crosslinking agents.

3.4 Stabilisation Against Burning and Chemical Agents

The $\text{OH}\cdot$ radicals are the most reactive of the active types formed during combustion of a hydrocarbon. They are responsible for the propagation of the flame, since they attack the neutral molecules of a hydrocarbon directly. Halogenated organic compounds are included in the polymer, in order to retard combustion. For a halogen, the efficiency of the retardant is inversely proportional to the energy of the R-X bond [82].



Other means are available for retarding combustion of the polymer, viz. protection by an inflammable coat which limits the diffusion of oxygen; the formation of an inflammable gas which dilutes the oxygen; and the promotion of endothermic reactions to reduce the temperature. The most common fire-retardant in polypropylene is a mixture of antimony oxide and halogenated compounds. Synergism has been detected between the antimony and the halogen, but the phenomenon has so far not been explained [83].

Polypropylene is stable against a large number of chemical products, with the exception of those with oxidising properties (H_2O_2 , HNO_3 , H_2SO_4 , etc.). Polypropylene swells by about 10% when brought into contact with common organic solvents, but is soluble at ambient temperature only in carbon tetrachloride and chloroform.

Manufacturers of polyolefins apply a surface treatment to reduce the permeability of the polymer, in order to protect the polyolefins against certain chemical agents.

4. PROPOSED PROGRAM FOR SOUTH AFRICA

Our proposed program for the stabilisation of polypropylene comprises three aspects:

1. A study of the influence of the dose and dose rate.
High dose rates can be reached with electron accelerators, and an investigation will be carried out to establish whether the formation of a strong local concentration of radicals favours their recombination. This problem was discussed earlier.
2. A search for new crosslinking agents.
The following are the new crosslinking agents to be tested: acetylene in combination with fluoroethylenes, solid derivatives of acetylene which can be added during melting, cyclopropane [84], methylvinylether [85] and unsaturated silanes [8,86].
3. A new approach to the post-irradiation phenomena.
The post-irradiation problem consists in destroying radicals with a long lifetime. This operation can be done chemically or by thermal annealing. The thermal conductivity of polypropylene is three times less than that of polyethylene, but the permeability of the two polymers is equal in respect of oxygen. Polypropylene is therefore less easily annealed. We propose to anneal irradiated polypropylene in a microwave oven in order to rapidly anneal the polymer to limit oxidative degradation. The heat no longer penetrates through the surface, but is rapidly generated within the dielectric material, and the polypropylene is also more sensitive to microwaves than is polyethylene [87].

5. EXPERIMENTAL SECTION

5.1 Nature and Purification of the Samples

The main characteristics of the polymer studied will be determined before each irradiation run. The insoluble residue obtained after extraction with n-heptane constitutes pure isotactic polypropylene [88]. The density is measured in a water-ethanol system or in a density-gradient column. The crystallinity is calculated by the Natta formula [89]:

$$\% \text{ crystallinity} = \frac{0,983 + 9 (t + 180)10^{-4} \cdot \left(\frac{1}{d}\right)}{4,8 (t + 180)10^{-6}}$$

where d is the density expressed in g/cm^3 at temperature t °C.

The degree of crystallinity can have a serious effect on the irradiation treatment. After Patel and Keller [90] had studied polyethylene crosslinking intensively, they came to the conclusion that crosslinking does not occur at random, but takes place in the amorphous region, in the fold surface between adjacent lamellae of the crystal, and at the ends of chains. The degree of crystallinity can also be measured with the aid of differential scanning calorimetry (DSC) curves in accordance with the following equation [91]:

$$100 \times \frac{\Delta H^*}{\Delta H_f} = \% \text{ crystallinity}$$

where ΔH^* = fusion heat of isotactic polypropylene
 ΔH_f = best value from literature for the extrapolated fusion heat (i-polypropylene : 50 ± 1 cal/g)

Since crosslinking occurs in the amorphous region of the polymer and on the surface of the crystals, the behaviour during irradiation will depend on the thermal treatment of the sample [92]. It is, in fact, the thermal aspect which determines the distribution, nature and degree of crystallinity in the polymer.

5.2 Irradiation Conditions

In keeping with the conditions of radiation sterilisation, the samples will be irradiated with cobalt-60 at doses of between 0 and 100 kGy (0–10 Mrad) and dose rates ranging from 1 to 40 kGy/h (0,1–4 Mrad). Higher dose rates can be achieved with an electron accelerator. The temperatures during irradiation will range from 10 °C to 50 °C. A study of polyethylene [93] revealed that the dose at gel point (r_g) and $G(X)$ is affected by the temperature.

The gaseous crosslinking agents will be added in variable quantities by a manometric method, although it will be difficult to handle these agents on an industrial scale. In order to ensure uniform distribution of the solid additives in the polypropylene, they must be added during fusion and must therefore be able to resist a temperature of 165 to 170 °C.

5.3 Molecular Masses

Polypropylene is susceptible to main-chain rupture, either directly as a result of the effect of radiation, or indirectly through the degrading effect of oxygen. The effect of radiation can therefore be observed by determining the molecular masses.

By measuring the osmotic pressure at a high temperature [94], the average-number molecular masses (\bar{M}_n) of the polypropylene can be calculated; they lie between 40 000 and 300 000. Membrane osmometry can be used at 130 °C, while 1,2,4-trichlorobenzene can be used as a solvent for the polypropylene [95].

The intrinsic viscosity can be used to follow the variation in molecular mass in irradiated polypropylene [96,97,98]. Keyzer, Clegg and Dole [99] obtain a linear relation between the intrinsic viscosity and the square root of dose (r), viz.:

$$\ln \frac{[\eta]_r}{[\eta]_0} = Ar^{1/2} + Br/2$$

where $[\eta]_r$ is the intrinsic viscosity at dose r , A is a constant and B virtually equals zero in the case of polypropylene. Kinsinger and Hughes [100,101] used the empiric equation of Mark Houwink to review the determinations of molecular masses from the intrinsic viscosity of polypropylene:

where exponent α is independent of the molecular mass distribution. In decahydronaphthalene (decaline), the exponent α has a value of 0,80 for polypropylene. In the case of a random distribution, the molecular masses follow the following relations [102]:

$$\bar{M}_n/\bar{M}_w \rightarrow 1/[(1 + \alpha) \Gamma (1 + \alpha)]^{1/\alpha}$$

where Γ represents the gamma function of $(1 + \alpha)$. Since $\alpha = 0,8$, we obtain $1/1,91/2$.

5.4 Differential-Scanning Calorimetry Measurements

The application of differential-scanning calorimetry (DSC) furnished numerous details on the modification of the solid state of polymers. Variations of the vitreous transition temperature, fusion temperature and fusion heat can be induced by radiation and detected by this method. Studies of polyethylene [92,103] prove that crosslinking increases in relation to the destruction of crystallinity. A linear depression of the fusion point of 0,3 °C per 10 kGy (Mrad) is observed for polypropylene [104], whereas this value is ten times smaller in the case of polyethylene. DSC measurements will be used to check the purity of the samples (presence of additives) and to attempt to detect the crosslinking brought about by some specific crosslinking agents.

5.5 Charlesby-Pinner Equation

$G(S)$, $G(X)$ and the dose at gel point (r_g) can be calculated by means of the equation which links the soluble fraction in xylene with the inverse of the dose.

r_g is calculated as follows [34]:

$$r_g = \frac{P}{2-1} = \frac{200 N_A}{\bar{M}_w [4 G(X) - G(S)]}$$

where P and l are the slope and the intercept of the straight line, respectively, defined by the equation of Charlesby and Pinner:

$$s + s^{1/2} = G(S)/2 G(X) + 100 N_A/r \bar{M}_w G(X)$$

The dose at gel point is important since it defines the efficiency of the crosslinking agent.

5.6 Post-Irradiation Effects

Geymer [9] stressed the importance of the post-irradiation phenomena. We shall attempt to determine the relative contribution of the post-irradiation reactions toward the overall modifications which are induced by ionising radiation in polypropylene. The residual radical can be destroyed quantitatively with the aid of thiols [105,106], in order to evaluate the variations of molecular masses as a

function of time and storage temperature. The -SH groups on the polymer can possibly be determined by infrared spectrometry.

5.7 Mechanical Tests

The mechanical tests will be conducted on an Instron Model 1026 apparatus for tensile strength tests, and on an Izod-type machine for the impact strength tests. Owing to the brittleness of polypropylene at low temperatures, these tests will also be carried out in the tough-brittle transition region. In order to take into account the influence of the flow-induced molecular orientation of actual mouldings (syringes), tensile impact will be investigated.

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ISBN 0 86960 649 2