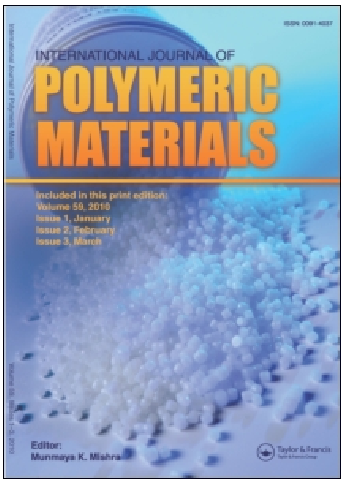

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A Controllable, Photodegradable Polyethylene Film for Agriculture

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INTRODUCTION

The tremendous expansion in the use of plastics as a packaging material in the 1960s, brought with it problems of garbage disposal and littering. The growing concern and awareness of pollution and other aspects of ecology, led plastics technologists and scientific workers to inquire into the possibilities of accelerated destruction of plastic waste. This was in contrast to previous industrial endeavours to prolong the service life of its products. Less than a decade later, it seems clear that, rather than cause the degradation and subsequent disintegration of the plastic materials, it is obligatory to conserve the material resources by recycling, regenerating or by reconstitution. Moreover, the thermal energy that can be recovered from plastics by burning is a considerable asset. Even if this were not so, it is a debatable point if induced accelerated degradability would be commercially attractive except for specific applications such as the one discussed here.

Photographs demonstrating the effectiveness of the films are included at the end of this paper.

THE AGRICULTURAL ASPECT

There is one field where the induced degradation of plastics can be of prime importance—in agriculture or that special sector of it which has become known as *plasticulture*. Plastic films and more specifically polyethylene films have brought about a veritable agricultural revolution. The various applications include mulching films, crop covers and fruit and crop protection as an aid towards advancing maturity and ripening, increasing yields, enhancing flavour, preventing blemishes, combatting diseases and pests, controlling the growth of weeds, conserving moisture and changing and modifying the microclimate of the soil and the space just above it. This is a formidable list and by no means complete. In arid and semi-arid regions it is the plastic films which make the growing of certain crops possible. In suitable regions for plasticulture, therefore, large quantities of polyethylene film are spread every year. The ensuing plastic residue represents not just an ecological nuisance, but it is a formidable agrotechnical obstacle. Unless removed, it will impede subsequent cultivation operations, obstruct machinery and hamper the growth of the following crop, wherever bits of film in the soil interfere with the emergence of the seedlings. It is therefore essential to remove the plastic film from the fields. It is an expensive, unattractive chore and the sheer bulk of the soiled films so collected make the option of regeneration a very doubtful one indeed. Even with the most efficient removal operation, enough bits of plastic film are left in the field, which continue to constitute an ever increasing pollution problem. It would be a boon to the agriculturist if he could be relieved of these problems by the disappearance of the films once they have served their purpose. The agriculturist is therefore quite willing to pay the additional expense for a degradable film, but on one condition only: the film must remain reliably in service during the period it has to perform its function. At the end of this time it must disintegrate quickly and totally.

It is with these demands in mind that controllable photodegradable films have been developed.

THE THEORETICAL BACKGROUND OF INDUCED DEGRADATION

The search for a source of energy for the initiation of a destructive process of the polymer structure has invariably led to the ever present abundance of solar irradiation.

Biodegradability offers poor prospects in so far as most plastic and polyethylene, in particular, are not wettable by water and do not lend themselves to microbiological attack. Specially built-in molecular structures have not led to significant results. Starchy fillers which have been proposed, weaken the mechanical properties of the films and also for reasons of controllability do not provide a reasonable solution.

Most of the work done so far has been concentrated on the use of sunlight for the degradative reactions, i.e. photodegradation. It is the ultra-violet region of the solar spectrum and especially the narrow band between 2950 Å–3200 Å that possess energies corresponding to the dissociation energies of the carbon–carbon bonds of the polymers. The well-known formula for the energy of a photon (quantum) is

$$E = h\nu = h\frac{c}{\lambda}$$

where h is Planck, s constant, ν is the frequency of monochromatic light, c is the speed of light and λ is the wave-length.

When expressed in kcal/mol, the following value is found, e.g.,

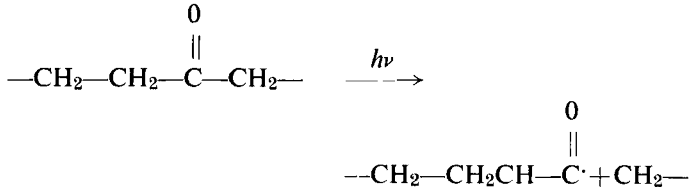
$$E = \frac{2.86 \times 10^5}{3000} = 95.3 \text{ kcal/mol}$$

Most of the bond energies of the carbon–carbon configurations lie in the vicinity of this value. (Table I). The processes of radiative degradation have been studied by many workers. Recent fundamental studies can be summarized as follows: A pure olefinic polymer—and here polyethylene as its most common representative shall always be meant—does not absorb ultra-violet radiation within the range obtained outdoors. That is from 2950 Å up to the visible light range starting from approximately 4100 Å. However, all polymers contain impurities introduced somewhere along the polymerization and manufacturing processes. Of importance are the carbonyl functional groups that are absorbing in the UV range up to 3400 Å. The resulting excitation leads to reactions generally known as Norrish Type I and Type II.[1]

TABLE I

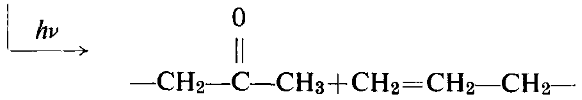
Dissociation energies of some hydrocarbon bonds

Bond broken	Bond energy kcal/mol (approx)
$CH_3—CH_3$	84
C—H	82
$CH_3—OH$	89
HCO—H	82
$CH_3CO—H$	88
$CH_3CO—OCH_3$	83
$CH_2—H$	86

I. 

$$—CH_2—CH_2—\overset{0}{\overset{\|}{C}}—CH_2— \xrightarrow{h\nu} —CH_2—CH_2CH—\overset{0}{\overset{\|}{C}}\cdot + CH_2—$$

II.



$$\xrightarrow{h\nu} -CH_2-\overset{\overset{0}{\|}}{C}-CH_3+CH_2=CH_2-CH_2-$$

Of special interest is the role of hydroperoxides as initiators of a free radical chain reaction.[2] The process of thermal and UV oxidative degradation being identical.

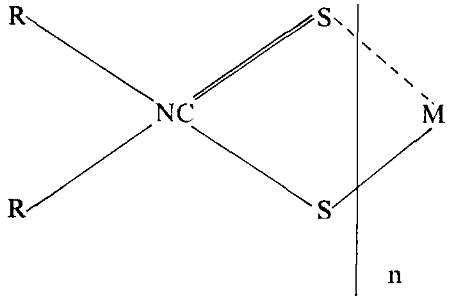
$$\left.\begin{array}{l} 2\,ROOH \longrightarrow ROO^\cdot + RO^\cdot + H_2O \\ \text{or}\quad ROOH \xrightarrow{h\nu} RO^\cdot + {}^\cdot OH \\ \left.\begin{array}{r} RO^\cdot \\ ROO^\cdot \\ {}^\cdot OH \end{array}\right\} + RH \longrightarrow \left\{\begin{array}{l} ROH \\ ROOH + R^\cdot \\ H_2O \end{array}\right. \end{array}\right\} \text{INITIATION}$$

$$\left.\begin{array}{l} R^\cdot + 0^2 \longrightarrow ROO^\cdot \\ ROO^\cdot + RH \longrightarrow ROOH + R^\cdot \end{array}\right\} \text{CHAIN REACTION}$$

$$2\,ROO^\cdot \longrightarrow \text{INERT PRODUCTS} \qquad \text{TERMINATION}$$

The overall effect of these reactions, as can be seen, are chain scission, unzipping chain reactions and crosslinking, all leading to the rapid reduction of the molecular weight of the polymer and with it the total loss of its mechanical strength, resulting in embrittlement.

Professor G. Scott of the Aston University in Birmingham, England, on whose work and patented method the technology presented here is based, has found a mechanism whereby the above-mentioned degradative processes can be usefully employed and controlled. It is well known that in order to counteract the degradation of polymers during processing and during outdoor exposure, certain stabilizing agents must be added. These stabilizers act variously in one or more specific ways, either as screening agents absorbing preferentially the potentially destructive radiation, or as energy transfer agents by accepting the energy of a donor molecule and dissipating it harmlessly as thermal energy. Another way is the scavenging action of deactivating free radicals or potential photo-activators, such as the hydroperoxides. It is the latter activity generally known as anti-oxidative which is of special interest. It has been found that certain metal organic complexes are useful anti-oxidants and hydroperoxide decomposers. Attention has been given to the metal dialkyldithiocarbamates, having this general configuration,



It is believed that the formation of sulphur dioxide is the reason for the powerful anti-oxidant property. Moreover the dithiocarbamates react rapidly with hydroperoxides at ambient temperatures. However, there is yet another aspect of the properties of the metal dialkyldithiocarbamates which rests on the fact of the presence of the transition metal atom. Such metal atoms present in a polymer matrix either by accident or purposely introduced, act as photo sensitizers when, on exposure to UV radiation the excited metal ions become catalytic activators, initiating the free radical chain reactions. It is with this in mind that further studies were conducted. It appeared that different transition metals whilst behaving in a similar manner under high temperature conditions acted in a different manner when exposed to UV radiation. The nickel and cobalt complexes showed stability on UV radiation whereas the ferric and copper complexes were rapidly destroyed by UV light. Laboratory experiments showed that by changing the concentration of the ferric dialkyldithiocarbamate in the polymer mass, a gradual change of the induction period was obtained. The metal complex acting as an initial stabilizer and then turning into a catalytic activator is in fact, a delayed action photo-activator. The chemical nature of the complex is favouring an auto accelerating free radical chain reaction. Employing these theoretical and laboratory findings it made it possible to produce a truly controllable photodegradable film (Figure 1). This film complies with most of the demands put upon it by the necessities of agricultural use.

PRACTICAL ASPECTS

Time control Ideally, the life span of the film should be controllable in such a way as to give induction periods that are shorter than the ordinary life span of an unmodified polyethylene, gradually lengthening to give a film which will last longer than the ordinary ones, in fact giving UV protection. This time control has been achieved. In practice, films with a minimal service time of seven weeks, up to films with an induction period of seven months have been

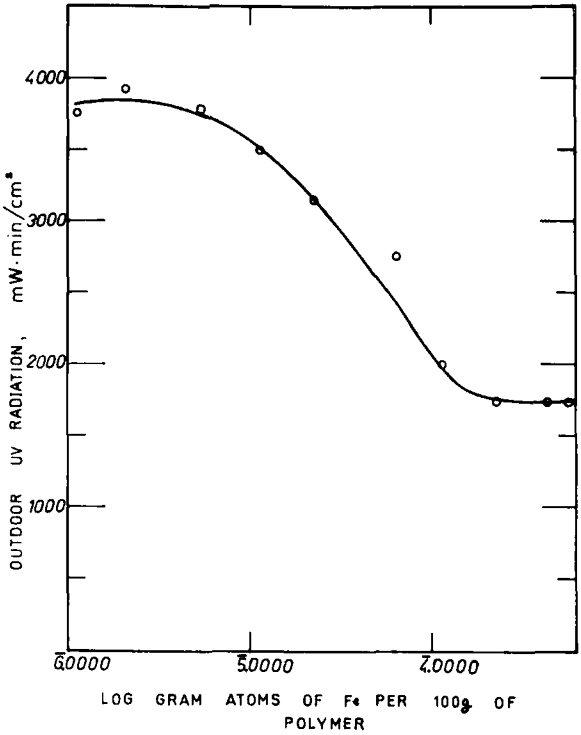


FIGURE 1 Irradiation of embrittlement vs. metal concentration.

successfully employed. The very strong sunlight in Israel is rather unvarying and its intensity during the annual cycle can be confidently predicted. It was, however, necessary to develop a technique based on thorough knowledge of the growing methods and characteristics of each crop. It can easily be seen that the growing crops will progressively shade mulching films from the sunlight, different crops providing different shading. Another factor is the widely differing irradiation at different times of the year (Figure 2). This can be used to good purpose by the fact that during sowing time and early development of the plants, very little UV radiation is incident on the films, so that climatic variations or those of the development of the plants have little or no effect on the overall dose of irradiation. However, as the season progresses UV radiation is intensified equalizing and overlaying any previously occurring deviations from the program.

Degradation In all cases, both in the short and the long induction period types of film, the original mechanical properties should be retained optimally until the end of the induction period. However, once the destruction mechanism

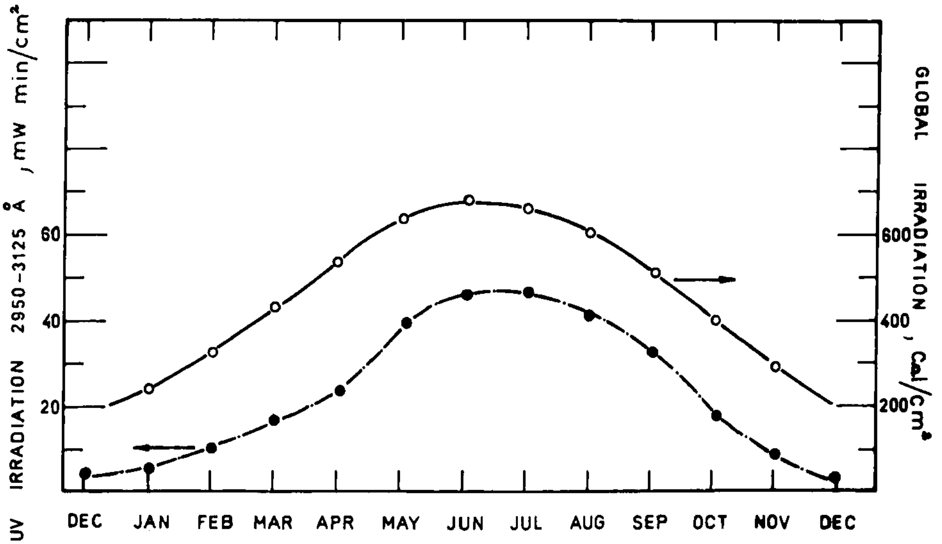


FIGURE 2 Average daily insolation in Israel.

takes over, the degradation should be rapid, total and be no longer dependent on the absorption of light.

The Scott type of photo-activators start an auto-accelerating process which breaks down the films into friable flakes which are no more troublesome to the farmer than dry leaves. This residue can now be ploughed under with impunity, the degradative process will continue in the dark in the presence of oxygen, albeit at a slower rate. Further breakdown will reduce the molecular weight to a point where the polymer will become wettable by water, but there is still little biodegradation. Only when the molecular weight falls below 5000, will biodegradation ultimately occur. It is at this point that the material will be effectively assimilated into the soil and into the carbon cycle of nature. An exact time-table for this process is indeed a subject for further study. The farmer, however, should be assured that no toxic or otherwise harmful residue remains in the soil and this seems to be an assumption well founded in fact and theory.

Storability The films should be unaffected by storage indoors, in the same way as are ordinary films. This presents no problems, as in keeping with most photo-sensitive polymers the activating wavelengths are not present indoors. UV light at the critical waveband does not penetrate window glass and is not generally reflected in diffused light. Ordinary storage procedure should therefore insure the retention of the original properties of the films.

Manufacturing and cost It would be desirable that the films should be easy to manufacture on ordinary extrusion machinery, the additives should be of the masterbatch type and be reasonably priced. All this in order to make the film an attractive proposition for the ultimate consumer; the farmer who will have to offset any extra cost by saving on the now redundant gathering-up operation.

Here again the new film meets all these requirements, the additives used are not much different from those in common use as UV stabilizers. Moreover, the metal complexes used are excellent heat stabilizers which are apt to produce films of higher quality than ordinary unstabilized films which are in general use in agriculture. Needless to say that the mechanical properties of the films are unaffected by the additives.

A NEW AGRICULTURAL GROWING METHOD

In Israel where the described degradable films have been developed, there are to-date already a number of crops that have been thoroughly studied and which are successfully grown by this new method. Melons and water-melons grown for export are planted early in February, at this time the seedlings have to be protected by plastic tunnels and the rows covered with mulching films. About 250 kilos of film per acre are needed. Photodegradable film has been used so far mainly for mulching, but there is no reason for not introducing it for the tunnels as well. The mulching films are spread mechanically in such a way that the edges are buried into the ground. The induction period is so timed that at the end of the growing period, i.e., May–June the films are already embrittled and are showing cracks and tears. After harvesting, the field is disc-harrowed in the direction of the rows, thereby burying some of the film that has been on top, but bringing up the edges that so far have been underground and were therefore unexposed to radiation. At this time of the year the radiation as well as the temperature are at their maximum. It is therefore obvious that the induction period will be very short and the newly exposed parts of the film will be quickly destroyed. The parts that are now underground will continue to break down in the manner described above.

Another and slightly different method is used in the growing of tomatoes for canning. These should be sown early to make full use of the canning facilities. Also, they must be grown on mulching films if top yields are desired. Tomatoes grown in this manner will yield over forty tons per acre or 350% more than without mulch. At harvesting time these heavy crops are profitably picked by self-propelled mechanical pickers that are in fact mobile packing stations having a crew of up to twenty sorters. The deployment of this labour-saving equipment is impossible for crops that are grown on plastic. The broad blade that cuts and lifts the vines whilst moving along the rows would be clogged immediately, making further progress impossible. Plastic film entering the separating mechanism would twist itself around moving parts. The degradable film at harvest time presents no such difficulty and will pass through the machine with the same ease as that of the leaves and vines of the crop. Here photodegradable film has opened a way for a hitherto prohibited technique.

There are many more crops that will shortly enter the sphere of photodegradable plastics. Crops that until now were excluded from regions, where the lack of moisture made the use of plastic mulch imperative, but at the same time harvesting methods prohibited it, can now be successfully grown.

CONCLUSIONS

After some years of experimentation a Scott-type photodegradable film is now commercially available in Israel. Already in its modest beginnings, it has drawn the attention of the agricultural community—farmers and researchers alike.

The successful application of the new plastic product promises to contribute significantly to the increase of food production, to the simplification of the growing technique and thereby lowering cultivation cost.

The new method will greatly reduce the littering and the pollution of the countryside and will keep the fields clean.

Thereby photodegradable agricultural film makes a significant contribution by increasing food production whilst keeping the fields and the countryside unpolluted in a self-cleaning process.

MULCHING OF BANANA SHOOTS WITH Plastor photodegradable film

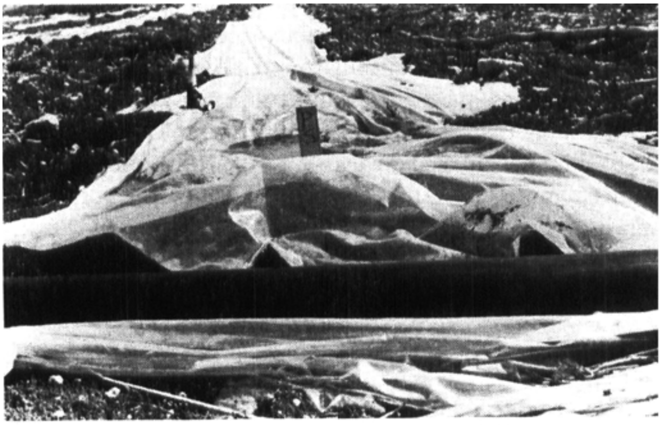
2. Film at the time of spreading, 25.3.72.

4. No sign of disintegration, 13.5.72.

6. Still no sign of disintegration, 2.7.72.

HOTODEGRADABLE POLYETHYLENE

Regular film "control"



1. Film at the time of spreading, 25.3.72.

3. Start of disintegration, 13.5.72.

5. Total disintegration, 2.7.72.

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