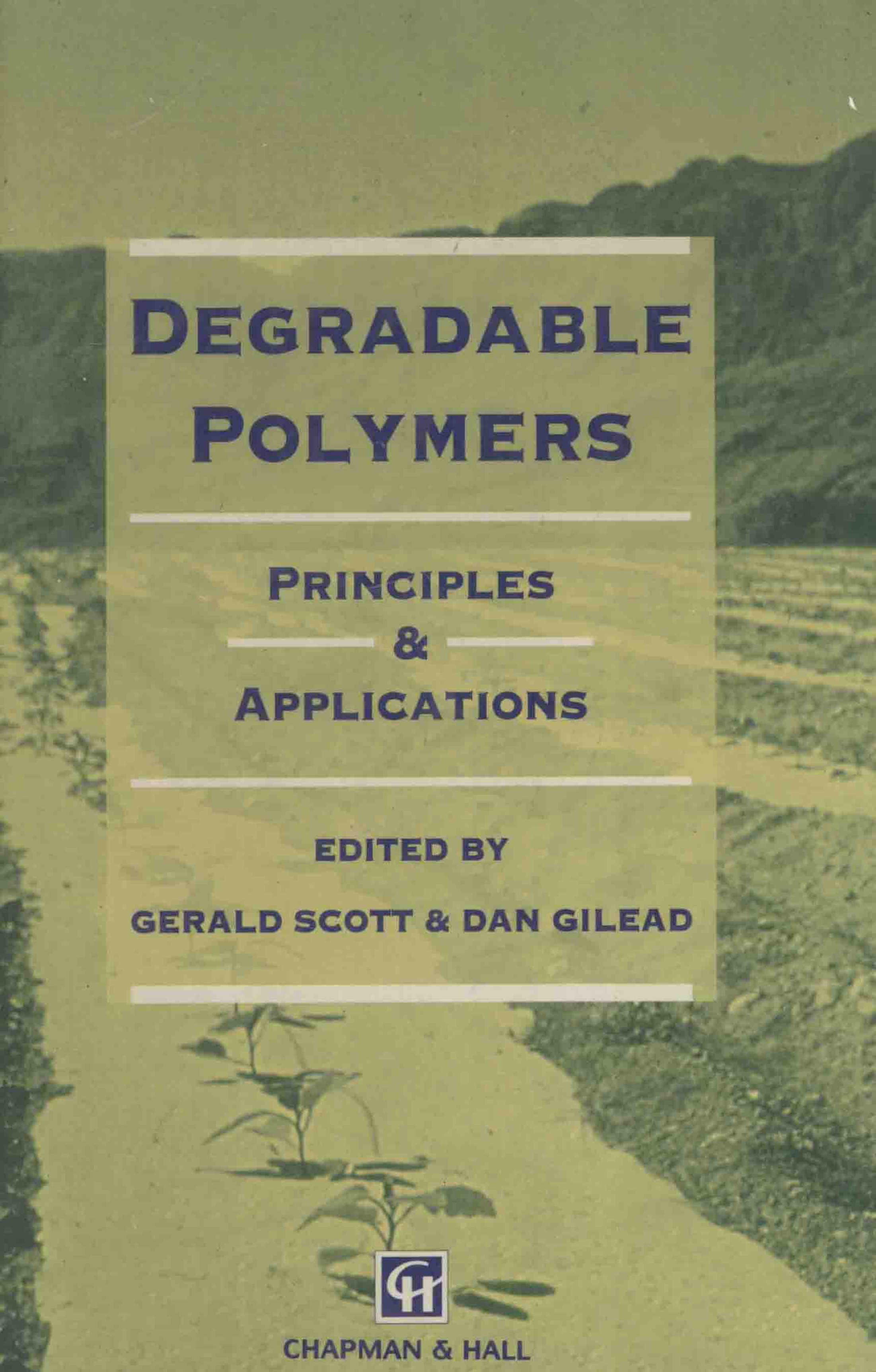

DEGRADABLE POLYMERS

PRINCIPLES & APPLICATIONS

EDITED BY

GERALD SCOTT & DAN GILEAD

CHAPMAN & HALL

Degradable Polymers

Principles and applications

Edited by

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Professor Emeritus in Polymer Science, Aston University, UK

and the late

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Founder and Director of the College of Plastics Technology of Israel

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Degradable Polymers

This book is dedicated to the memory of
Dan Gilead

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Preface

Few scientific developments in recent years have captured the popular imagination like the subject of 'biodegradable' plastics. The reasons for this are complex and lie deep in the human subconscious. Discarded plastics are an intrusion on the sea shore and in the countryside. The fact that nature's litter abounds in the sea and on land is acceptable because it is biodegradable – even though it may take many years to be bioassimilated into the ecosystem. Plastics litter is not *seen* to be biodegradable and is aesthetically unacceptable because it does not blend into the natural environment. To the environmentally aware but often scientifically naïve, biodegradation is seen to be the ecologically acceptable solution to the problem of plastic packaging waste and litter and some packaging manufacturers have exploited the 'green' consumer with exaggerated claims to 'environmentally friendly' biodegradable packaging materials. The principles underlying environmental degradation are not understood even by some manufacturers of 'biodegradable' materials and the claims made for them have been categorized as 'deceptive' by USA legislative authorities. This has set back the acceptance of plastics with controlled biodegradability as part of the overall waste and litter control strategy.

At the opposite end of the commercial spectrum, the polymer manufacturing industries, through their trade associations, have been at pains to discount the role of degradable materials in waste and litter management. This negative campaign has concentrated on the supposed incompatibility of degradable plastics with aspects of waste management strategy, notably materials recycling.

Between the two extremes outlined above lie several areas of application of degradable polymer technology which do not attract the same emotive reactions from environmental or recycling campaigners, but which are already bringing considerable social and economic benefits. The first is the use of time-controlled degradable polyolefins in agriculture (mulching film, netting, twine, etc.) where great benefits have already been achieved in increased crop yields and reduced crop management costs. The second is in biomedical applications where synthetic resorbable polyesters are being used in sutures, implants, etc. to support the body's recovery systems. Another is the rapidly developing interest in the use of polymers with time-controlled degradation for controlled release of fertilizers, pesticides, *in vitro* and drugs, nutrients, etc. *in vivo*. It is in these non-packaging uses of degradable polymers that most progress has been made in understanding the scientific principles involved and the first objective of this book is to outline this progress. It can now be seen that the sharp distinction formerly made between abiotically and biotically degradable polymers was somewhat artificial and not helpful to the understanding of how synthetic polymers are absorbed into their environment. Both involve an abiotic and biotic stage and the overall rate of bioassimilation is generally controlled by the former. A second objective is to reconsider the problems of plastics waste and litter control in the light of the synthetic polymer ecobalance. The chemistry and biology of polymer degradation is now sufficiently well understood to allow us to see how controlled degradability can enhance the systems approach to waste and litter management.

Dan Gilead, my co-editor and colleague, was a pioneer of the use of degradable polymers in agriculture. Unfortunately Dan died suddenly before the book could be completed. As well as being an irreplaceable loss to the plasticulture industry which he pioneered, his friendship and enthusiasm will be greatly missed by his scientific collaborators and industrial competitors alike. This book which he instigated is a tribute to the part he has played in the application of degradable polymers to important social concerns.

Gerald Scott
Birmingham UK
July 1994

Contents

Introduction to the abiotic degradation of carbon chain polymers

1

Gerald Scott

SUMMARY

The oxidation of the hydrocarbon polymers begins during processing (mechanooxidation), and the formation of hydroperoxides during fabrication of polymers affects the rate of thermo- and photooxidation of the polyolefins during subsequent use (aging and weathering). The end products of thermal and photooxidation are low molecular weight carboxylic acids which are involved in the eventual bioassimilation of the polymers in the ecosystem.

Antioxidants (processing stabilizers) are used to limit degradation during manufacture and heat and light stabilizers to control the rate of environmental oxidation and ultimately biodegradation. The mechanisms by which antioxidants and light stabilizers act are outlined.

1.1 ABIOTIC POLYMER DEGRADATION: PRECURSOR TO BIODEGRADATION

Most synthetic carbon-based polymers are inert toward micro-organisms in the form in which they are initially produced. In order that the carbon nutrients which they contain can be made available to the biological cell, they must be first transformed by a variety of chemical reactions to low molecular weight metabolites that can be absorbed by the cell [1]. These reactions are sometimes induced by oxidative enzymes, following the colonization of cells on the surface of the polymer. This is in turn followed by surface erosion [2]. However, biodegradation does not need to be enzymically induced and in most cases is not [3] and the rate of the initiation process is governed by the normal abiotic mechanisms of organic and physical chemistry.

Abiotic reactions which lead to the formation of cell nutrients at ambient temperatures fall into two main chemical classes; namely, hydrolysis and

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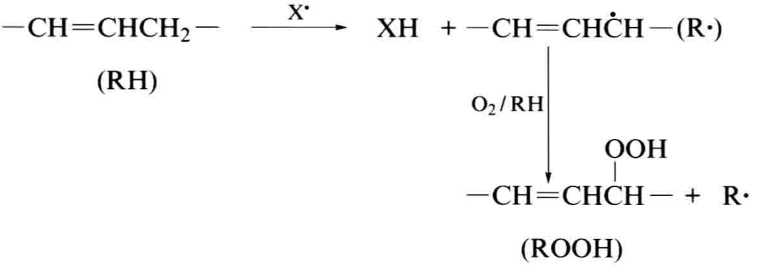
autoxidation [4]. The first occurs primarily with the heterochain polymers, the polyesters, polyamides and polyurethanes and is discussed in considerable detail by Li and Vert in Chapter 4. The second is the predominant initiating reaction in the bioassimilation of the water-resistant polymers, notably the carbon chain polymers [3]. However, although one chemical agent may dominate in any particular case, it is not necessarily exclusive of the alternative process and some polymers, for example, the polyether polyurethanes may degrade abiotically by both hydrolysis and oxidation [5, 6]. Furthermore, the nature of the chemical process may change during the progress of the degradation. For example, esters are major products of the photo-oxidation of hydrocarbon polymers (see below), but these are almost certainly hydrolysed to the free carboxylic acids before being bioassimilated by the 'β-oxidation' process. Conversely, it has been shown that prior photooxidation may increase the rate of fungal hydrolysis of the polyurethanes, by reducing the molecular weight of the polymer [7].

As a result of the intensive studies of both polymer hydrolysis and polymer oxidation in recent years, it has become evident that the rate of the chemical initiating step is dominated by the physical accessibility of the polymer structure to the abiotic attack. Thus for example, the crystallinity of the polyesters strongly influences their rate of hydrolysis due to the impermeability of the crystalline regions to water [2]. Hydrolysis is therefore initially restricted to the amorphous phase and to the fringes of the crystallites. Entirely analogously, oxidation of the polyolefins occurs almost exclusively in the amorphous region of the polymer since the crystallites are impermeable to oxygen [8]. Consequently, the highly crystalline polymers are relatively resistant to oxidation [9]. In both cases, breaking of the 'tie-bonds' between the crystallites leads to 'chemicrystallization' and physical disintegration of the polymer artefact. Subsequent chemical and biological assimilation processes are controlled by the competition between the increased surface area of the polymer and the decreased chemical accessibility of the crystalline residue, Although this means that the crystalline polymers are initially relatively resistant to abiotic attack, it does not follow that they retain their physical integrity longer than the more chemically susceptible polymers. In fact the reverse is normally the case [10], since the destruction of the amorphous phase reduces impact strength and leads to more rapid physical disintegration the higher the crystallinity of the polymer [11]. However, once fragmentation has occurred, the surface area available for further oxidation and hence biodegradation is considerably increased and autoaccelerating degradation occurs.

A distinction is sometimes drawn between 'biodegradable' and 'nonbiodegradable' polymers, but the above arguments indicate that the difference lies in the rates of the abiotic processes which precede biological attack. For example, the polyunsaturated elastomers are very susceptible to biodegradation in the form of latex. This is because the hydrocarbon structure is extremely readily oxidized by oxygen of the atmosphere to low molecular weight aldehydes and acids [11] which are readily bioassimilated. By contrast, polyethylene terephthalate is very resistant to biodegradation because of its high crystallinity and resistance to hydrolysis. Unlike latex, vulcanized rubbers, when fully formulated with antioxidants, compare with the crystalline polyesters in their resistance to biodegradation. This is evidenced in the number of discarded tyres which survive for decades in the outdoor environment. The bioresistance of the automobile tyre, therefore, has much more to do with its formulation to resist oxidation than with the inherent resistance of the polyunsaturated polymer to biodegradation. The hydrolytic resistance of the condensation polymers is to a large extent controlled by the polymer morphology and hence by the access of water to the reaction site. By contrast, as will be seen below, the control of oxidation of the carbon chain polymers by antioxidants and stabilizers provides a very effective and versatile means of controlling their biodegradability. The time-controlled biodegradation of the polyolefins using this principle will be discussed in detail in Chapter 9. The main purpose of the following sections is to provide the mechanistic background to the oxidation chemistry involved.

1.2 ENVIRONMENTAL OXIDATION OF POLYMERS

The oxidation of a polymer is dependent both on its chemical structure and on its morphology [4, 9]. In general the polyunsaturated rubbers are very susceptible to oxidation due to the presence of the olefinic double bond in the polymer back-bone and the absence of crystallinity. They are autoxidized by the well-known radical chain reaction summarized in reaction (1.1) [12];

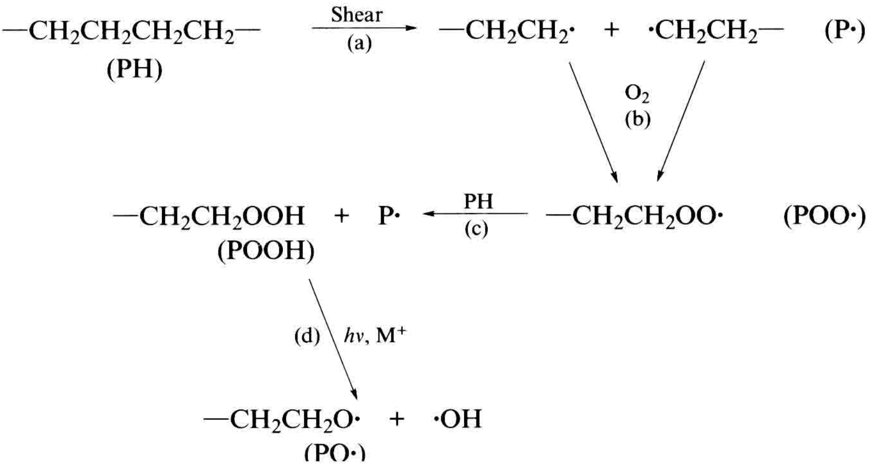


$$\begin{array}{ccl} \underset{(RH)}{-CH{=}CHCH_2-} & \xrightarrow{X^\cdot} & XH + -CH{=}CH\dot{C}H-(R\cdot) \\ & & \quad\big\downarrow{\scriptstyle O_2/RH} \\ & & \underset{(ROOH)}{-CH{=}CH\overset{OOH}{C}H- + R\cdot} \end{array} \qquad (1.1)$$

where X is an 'oxyl' radical.

The polyolefins, which contain relatively few double bonds are much more stable and their inherent oxidizability depends on the number of tertiary carbon atoms in the chain; the order of oxidizability is therefore polypropylene (PP) > low density polyethylene (LDPE) > high density polyethylene (HDPE) [9]. However, HDPE and PP have a higher degree of crystallinity than LDPE and for the reasons discussed above, they undergo chemicrystallization and embrittlement more rapidly than LDPE. Electron-attracting groups in the polymer chain or pendant to the polymer chain increase oxidative stability, so that the carbonyl-containing polymers (polyamides, polyesters, acrylics, etc.) and the halogenated polymers are relatively stable to oxidation [4]. Polytetrafluoroethylene (PTFE) is extremely resistant to oxidation and does not biodegrade because it does not contain a carbon—hydrogen bond and cannot therefore undergo hydrogen abstraction by reaction (1.1).

Pure polymethylene, —$(CH_2)_n$—, is much more resistant to oxidation than the commercial polyethylenes. There are two reasons for this. The first is that the latter contain some olefinic unsaturation introduced during synthesis and the second and more important reason is that screw extrusion of polymers in the viscous molten state at high temperatures in the presence of oxygen chemically modifies polymers by the introduction of sensitizing oxygen-containing species [13]. The mechanochemical reaction which results from shearing of the polymer chain is typified for polyethylene in Scheme 1.1. Hydroperoxides produced in the polymer at this stage subsequently sensitize the fabricated product to oxidation unless steps are taken to minimize oxidation by the use of antioxidants (see Section 1.3).



Scheme 1.1 Mechanooxidation of polyethylene during processing.

Hydroperoxides decompose relatively slowly at ambient temperatures in the dark, but in light they are readily photolysed to free radicals, (Scheme 1.1, reaction d). Consequently, the rate of photo-oxidation of the hydrocarbon polymers is orders of magnitude higher than thermal oxidation. In addition, small amounts of transition metal compounds, notably iron, cobalt, manganese and copper, have a powerful catalytic effect on radical formation from hydroperoxides [14], leading to rapid molecular weight reduction by breakdown of the intermediate alkoxyl radical and the formation of carboxylic acids and esters as oxidation end products (see Scheme 1.2) [15].