

Oxidative degradation and stabilisation of polymers

S. Al-Malaika

The aim of this review is to present a coherent treatment of the fundamental aspects of the science that underpins current technological practices, and future advances, in the stabilisation of synthetic organic polymers. Aspects of polymer oxidation are introduced first before discussing the role of antioxidants, with numerous examples, to illustrate their basic mechanisms of action. The state of the art is discussed with particular emphasis on recent development and progress.

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Introduction

Organic materials are susceptible to attack by atmospheric oxygen. In the case of synthetic organic polymers, molecular oxygen initiates oxidative degradation processes that lead to material failure. Polymer oxidation is often accelerated by other environmental, biological and physical factors, e.g. sunlight, ozone, heat, radiation, mechanical stress, traces of transition metal ions, water, pollutants and micro-organisms. Oxidative degradation of commercial organic polymers occurs, to varying degrees, at every stage of their lifecycle, including manufacture, processing, fabrication, storage and in-service, both during their first and subsequent (i.e. after recycling) lifetimes. Such oxidative processes lead to the irreversible deterioration of the useful properties (e.g. mechanical properties; tensile, flexural and impact strengths; surface appearance; gloss, texture, and colour) of polymer artefacts and are reflected in poor performance or catastrophic failures. The extent of oxidative degradation, however, is not the same in all polymers; it depends on intrinsic chemical structure (with concomitant chemical and physical structural defects) and susceptibility to external influences during the lifetime of the polymer product.

The early searches for 'antioxidants' were empirically based and have led to the production of a number of inhibitors of oxidation.¹⁻³ Subsequent development focused on understanding of the underlying processes of oxidation and inhibition in polymers.⁴⁻⁶ A further intense period of research ushered in a new era where an understanding of basic mechanisms of action of polymer oxidation and commercial antioxidants has transformed the trial and error practices of industry to a mature science based polymer stabilisation technology.⁷⁻¹²

The terms stabilisers and antioxidants are generally used in the plastics industry to describe chemical

agents that combat and inhibit the combined degradative effects of oxygen, temperature and light. The terms primary and secondary antioxidants are also used sometimes even though the distinction is rather arbitrary and does not relate to their mechanisms of action. On the other hand, the rubber industry tends to use terms such as antidegradants, antifatigue agents and antioxidants, to refer similarly to chemical agents that act against the deleterious effects of temperature, stress and ozone, respectively. Although antioxidants and stabilisers are normally used at low concentrations (generally < 1%) they are key ingredients in the compounding of polymers. The continuous growth of polymer markets has ensured a parallel growth in the demand for antioxidants and stabilisers, especially in the large tonnage polymers with major packaging, building, automotive, electrical and electronics applications.

Autoxidation of polymers

Synthetic organic polymers are susceptible to attack by molecular oxygen in an autocatalytic reaction; hence the term *autoxidation*¹³⁻¹⁶ is used to describe an oxidation reaction that starts slowly, possibly with a short induction period, followed by a gradual increase in the rate (ascribed to the build up of hydroperoxides) which eventually subsides giving rise to a sigmoidal curve. The length of the induction period is very short or absent when initiators (e.g. peroxides, azo compounds) are present, but can be prolonged in the presence of antioxidants and stabilisers (Fig. 1). The basic autoxidation theory of hydrocarbons which involves a complex set of elementary reaction steps is similarly valid for polymer oxidation.^{4,17-19} The role of hydroperoxides formed during autoxidation of polymers cannot be overemphasised; they are associated with further initiation, changes in molar mass and other polymer properties leading ultimately to loss of properties and catastrophic failure (see Fig. 2). Studies of oxidation in polymers, both in the solid phase (e.g. under service conditions in the presence of heat or light) and in the viscous melt during processing, have been shown to be more complex than in liquid hydrocarbons due to problems of oxygen diffusion, solubility, and effects of polymer crystallinity and morphology.^{20,21} For example, oxygen solubility in solid polymers (e.g. polyolefins) is not greatly different (slightly lower) from that in liquid hydrocarbons, whereas its diffusion in polymers is two orders of magnitude slower.²⁰

The *autoxidation* process of polymers involves free radical initiated chain reactions and proceeds in three basic steps: initiation, propagation and termination (Scheme 1).¹⁷ Many factors, e.g. heat, mechanical stress, light and transition metal impurities, contribute to the initiation step leading to the formation of the first alkyl macroradicals (Scheme 1, reaction 1). Bimolecular oxygen-polymer reaction is generally not

Degradation And Stabilisation Of Polymers

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Degradation And Stabilisation Of Polymers:

Polymer Degradation and Stabilisation Norman Grassie, Gerald Scott, 1988-04-14 The study of polymer degradation and stabilisation is of considerable practical importance as the industrial uses of polymeric materials continue to expand In this book the authors lucidly relate technological phenomena to the chemistry and physics of degradation and stabilisation processes Degradation embraces a variety of technologically important phenomena ranging from relatively low temperature processes such as weathering of plastics fatigue of rubbers through the processing of polymers in shearing mixers to very high temperature processes such as flammability and ablation All these technological phenomena have in common certain basic chemical reactions Thus weathering has its roots in photo oxidation fatigue and melt degradation in mechano oxidation and flammability and ablation in ablation in pyrolysis and vapour phase oxidation

Polymer Degradation and Stabilization W. L. Hawkins, 2012-12-06 The development of polymers as an important class of material was inhibited at the first by the premature failure of these versatile compounds in many applications The deterioration of important properties of both natural and synthetic polymers is the result of irreversible changes in composition and structure of polymers molecules As a result of these reactions mechanical electrical and or aesthetic properties are degraded beyond acceptable limits It is now generally recognized that stabilization against degradation is necessary if the useful life of polymers is to be extended sufficiently to meet design requirements for long term applications Polymers degrade by a wide variety of mechanisms several of which affect all polymers through to varying degree This monograph will concentrate on those degradation mechanisms which result from reactions of polymers with oxygen in its various forms and which are accelerated by heat and or radiation Those stabilization mechanisms are discussed which are based on an understanding of degradation reaction mechanisms that are reasonably well established The stabilization of polymers is still undergoing a transition from an art to a science as mechanisms of degradation become more fully developed A scientific approach to stabilization can only be approached when there is an understanding of the reactions that lead to degradation Stabilization against biodegradation and burning will not be discussed since there is not a clear understanding of how polymers degrade under these conditions

Degradation and Stabilisation of Polymers G. Geuskens, 1975 **Fundamentals of Polymer Degradation and Stabilization** N.S. Allen, M. Edge, 1992-10-31 During the past decade the field of polymer degradation and stabilization has become a subject of central importance in polymer science and technology This book provides a fundamental source of information designed for those with only a basic understanding of the background of the field **Degradation and Stabilization of Polymers** Hans Helmut Gunter Jellinek, 1983 *Mechanisms of Polymer Degradation and Stabilisation* G. Scott, 2012-12-06 The purpose of this publication is two fold In the first place it is intended to review progress in the development of practical stabilising systems for a wide range of polymers and applications A complementary and ultimately more important objective is to accommodate these practical developments within the framework of antioxidant theory since

there can be little question that further major advances in the practice of stabilisation technology will only be possible on a firm mechanistic foundation. With the continual increase in the number of commercial anti oxidants and stabilisers often functioning by mechanisms not even considered ten years ago there is a need for a general theory which will allow the potential user to predict the performance of a particular antioxidant structure under specific practical conditions. Any such predictive tool must involve a simplified kinetic approach to inhibited oxidation and in Chapter 1 Denisov outlines a possible mechanistic approach with the potential to predict the most useful antioxidant to use and the limits of its usefulness. In Chapter 2 Schwetlick reviews the current state of knowledge on the antioxidant mechanisms of the phosphite esters with particular emphasis on their catalytic peroxidolytic activity. Dithiophosphate derivatives show a similar behaviour but for quite different reasons and in Chapter 3 AI Malaika reviews information available from analytical studies particularly using ^{31}P NMR spectroscopy to elucidate the complex chemistry that leads to the formation of the antioxidant active agents.

Polymer Degradation and Stabilization W. Lincoln Hawkins, 1984

Thermal Stability of Polymers T. R. Crompton, 2012-05-08

In recent years numerous research papers have been published on the changes in chemical structure and in physical properties of polymers when they are exposed to heat over a range of temperatures. For example these changes can occur at any time during the injection moulding of the plastic in the subsequent processing and in its end use application when exposed to elevated temperatures. Thermal stability is a very important parameter which must be taken into account when selecting polymers whether for their use as constructional or engineering applications or in the packaging of food at high temperatures. The mechanisms by which such changes occur are many and it is important to know what these are and to be able to measure the rate of change of polymer structure and its dependence on temperature and time. Development of an understanding of the mechanisms of thermal degradation will help the chemist to develop materials with better thermal stability. This is particularly important in newer developments in engineering and aerospace. This book reviews in nine chapters the measurement of these properties in the main types of polymers in use today. Numerous techniques are discussed ranging from thermogravimetric analysis differential scanning calorimetry infrared and nuclear magnetic resonance based methods to pyrolytic techniques such as those based on pyrolysis gas chromatography and mass spectrometry. The book is aimed at those engaged in the manufacture of polymers and the development of end use applications. It is essential that students of polymer science should have a thorough understanding of polymer stability and an additional aim of the book is to help in the development of such an interest.

Aspects of Degradation and Stabilization of Polymers Hans Helmut Gunter Jellinek, 1978

Degradation and Stabilisation of Polyolefins Norman S. Allen, 1983

Thermal Degradation of Polymeric Materials Krzysztof Pielichowski, James Njuguna, Tomasz M. Majka, 2022-11-05

Thermal Degradation of Polymeric Materials Second Edition offers a wealth of information for polymer researchers and processors who require a thorough understanding of the implications of thermal degradation on materials and product

performance Sections cover thermal degradation mechanisms and kinetics as well as various techniques such as thermogravimetry in combination with mass spectroscopy and infrared spectrometry to investigate thermal decomposition routes Other chapters focus on polymers and copolymers including polyolefins styrene polymers polyvinyl chloride polyamides polyurethanes polyesters polyacrylates natural polymers inorganic polymers high temperature resistant and conducting polymers blends organic inorganic hybrid materials nanocomposites and biocomposites Finally other key considerations such as recycling of polymers by thermal degradation thermal degradation during processing and modelling are discussed in detail Explains mechanisms of polymer degradation making it possible to understand and predict material behavior at elevated temperatures Offers systematic coverage of each polymer group that is supported by data detailed explanations and critical analysis Investigates thermal decomposition routes in new materials such as organic inorganic hybrid materials and polymer nanocomposites

Degradation of Polymers R.G. Compton,C.H. Bamford,C.F.H. Tippert†,1975-01-01 Degradation of Polymers *Polymer Degradation and Stability Research Developments* Leo B. Albertov,2007 Polymer degradation is a change in the properties tensile strength colour shape etc of a polymer or polymer based product under the influence of one or more environmental factors such as heat light or chemicals This book presents research in this field *Environmental aspects of the degradation and stabilisation of polymers* ,1990 **Weathering of Polymers** S.M. Halliwell,1992 This report describes the theory of weathering and its effect on polymer properties methods of stabilisation and natural and accelerated weathering tests The problems associated with particular polymers used in outdoor applications are explained An additional indexed section containing several hundred abstracts from the Rapra Polymer Library database provides useful references for further reading Reactive Modifiers for Polymers S. Al-Malaika,1997-06-30 There is considerable interest within the polymer industry in developing methods to modify existing polymer systems to achieve improvements in their functional or engineering properties The chemical treatment of polymers either prior to or during processing represents an inexpensive and rapid way of achieving these modifications and a great deal of research is underway directed at improving both the understanding of the processes involved and the development of the practical techniques employed The improvements obtained by chemical treatment range from subtle alteration of the chemical properties of a polymer to wholesale changes in the physical mechanical and chemical properties with the current favourable economics ensuring that industry will continue to exploit the technique in the search for improved polymer materials Written by an international team of authors drawn from both basic and applied research programmes in industry and academia and with a strong emphasis on the underlying chemistry this book forms a timely concise and accessible evaluation of the most promising technologies developed to date Chemists technologists materials scientists and engineers working in all areas of the polymer industry along with academic researchers in those fields will find this book an essential source of reference in the course of their work **Stabilization of Polymeric Materials** Hans Zweifel,2012-12-06 Plastics are used worldwide in

everyday life e g as food packaging electronics construction automotive parts and household appliances To produce these products with the desired service lifetimes the use of suitable stabilizers is necessary This book provides a concise and comprehensive overview of the basic mechanisms of plastic degradation processes caused by heat and light At its core is a detailed description of the stabilization of different polymers including an explanation of stabilization mechanisms and the influence of commonly used additives such as fillers flame retardants and pigments on the stability of plastic Every polymer scientist material technologist or application engineer dealing with the design of the properties of plastics will benefit from this new overview

Handbook of Polymer Degradation S. Halim Hamid,2000-06-30 Covers recent advances in polymer degradation and stabilization Focuses on the basics of photo and bio degradability Delineates special and general environmental parameters such as solar irradiation temperature and agrochemical exposure Surveys plastic waste disposal strategies such as recycling incineration chemical recovery by pyrolysis and source reduction

Polymer Stabilisation Mechanisms and Applications N. C. Billingham,D. M. Wiles,1991 *Degradation, Stabilization, and Recycling of Packaging Materials* Muhammad Rabnawaz,Susan E. M. Selke,Ian Wyman,2025-04-29 Practical guidance to sustainable packaging and its challenges with analysis of various packaging materials and their interactions with different environments

Degradation Stabilization and Recycling of Packaging Materials analyzes packaging materials and their interactions with different environments discussing the degradation processes of different materials like plastics wood paper glass and metal providing specific strategies to address these degradation processes and exploring solid waste management recent developments in recycling and the principles of eco friendly packaging design Organized into two parts the first section of this book provides a comprehensive examination of how environmental factors such as heat shear light air packaged products and stress affect packaging materials focusing on the chemistry of their deterioration and stabilization methods The second section explores solid waste management recent developments in recycling and key principles of eco friendly packaging design culminating in an extensive discussion of legal and regulatory aspects The book includes case studies and problem sets in each chapter with solutions to the problems in an appendix in the back of the book Written by a team of highly qualified authors

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Degradation Stabilization and Recycling of Packaging Materials is a critical resource for researchers students and industry professionals in the field of materials science and packaging to evaluate challenges related to solid waste and devise

effective disposal strategies

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