General Introduction

Why oxidation?

The yellowing of a polyester-fiberglass hull, the crumbling of paint, the development of a purple coloration at the surface of a PVC extrudate for building are all manifestations of oxidative ageing of polymers. These are examples of changes in the visual aspect of the materials, which may have significant financial consequences but which do not, in themselves, pose a threat to the safe use of the system in question. The embrittlement of a carbon-polyimide part functioning at 200°C in an airplane engine, the hardening of a polybutadeine matrix rocket propeller, and the cracking of a polyethylene electrical cable sheath in a nuclear plant, are also manifestations of oxidative ageing of polymers, but here the resulting failures could have grave consequences on every level. Predicting failures is the main objective of ageing studies. What fails is a system, a structure (in the broader sense). In certain cases, this failure is related to an unforeseen change in the operating conditions (an accident, a fire, etc.). In others, it is related to an inadequate knowledge of the system's capacity to withstand the mechanical loads to which it is subjected (creep, fatigue, etc.). These failures may also result from two incompatible materials being brought into contact, or one material coming into contact with incompatible fluids. Here, we look only at the case of a system failure resulting from the change in the properties of one of its constituent materials, and that change resulting from that material interacting with oxygen. We shall focus on deterministic approaches to the problem, i.e. cases where the system failure can be associated more-or-less accurately with a critical structural state of the material, or at the very least with a critical value of a property of the material. Why limit ourselves to the study of oxidation? For the simple reason that if we lived in a neutral atmosphere, 99% of thermal or photochemical ageing problems would disappear, with the lifespan of polymers being many times higher than it is in the presence of oxygen. However, in many cases oxidation takes place alongside other types of ageing, and there may be significant interplay between these different phenomena. For example,

the performances of an antioxidant depend as much on its resistance to migration as on its chemical reactivity; it is therefore impossible to ignore the phenomena of transport of stabilizers (and of all reactive substances including, of course, oxygen), even if these phenomena exist independently of oxygen.

A brief history

As a scientific discipline, the oxidative ageing of polymers has been studied since the mid-19th Century, i.e. a little after the invention of vulcanization of rubber (Goodyear 1839). It immediately became apparent that natural rubber quickly lost its mechanical properties because of oxidation, and that discovering ways to stabilize it was a crucially important objective for research. The first patent on an antioxidant dates from the 1860s. During the earlier half of the 20th Century, the oxidation of rubber was the subject of numerous works, sometimes by very renowned authors – e.g. in France: Moureu, Dufraisse, Lebras, etc. However, they lacked the essential theoretical tools to reach a sufficient level of understanding. These tools essentially stem from macromolecular physical chemistry, established by Staudinger (Nobel Prize, 1953) between 1925-1930, and radical chain reaction kinetics, established around the same time by Semenov (Nobel Prize 1956). The modern view of oxidation kinetics developed by Semenov and his students (Emanuel, Denisov, etc.) was discovered in the western world after the Second World War by an English team from RAPRA [BOL 46a]. In normal conditions of thermo-oxidation, the kinetics are highly non-linear because the chain reaction produces its own initiator: the hydroperoxide group, the accumulation of which is responsible for the acceleration observed. Tobolsky *et al.* in 1950 developed an extremely pertinent model to account for this type of behavior. Unfortunately, and inexplicably, this model remained unknown to the scientific community, and apparently even to Semenov [SEM 59], for nearly half a century. Researchers came up against another hurdle: controlling the kinetics by oxygen diffusion, leading to an oxidation gradient within the thickness of the samples. Although solutions existed, they were unknown to the polymer oxidation community until the start of the 1980s. Between 1945-1980, researchers would limit themselves to studying cases where the above difficulties are avoided: constant initiation rate leading to linear kinetics, thin samples in order to minimize the gradients and oxygen excess to simplify the mechanistic schemes. Research focused, essentially, on analyzing the reaction products, determining the elementary rate constants and developing theoretical and experimental tools to look at the effects of ageing on macromolecular structure. Besides Bolland and Tobolsky, mentioned above, Mayo, Howard, Ingold, Uri, Reich, Stivala, Hawkins, Charlesby, Kamiya, Emanuel, Denisov, Kuzminskii and Shlyapnikov are among the authors most frequently cited from this period.

The earliest models of oxygen-diffusion-controlled kinetics appeared in the early 1980s in Japan [SEG 81] and Britain [CUN 82], which would later be drawn heavily upon by Gillen and Clough in the USA [GIL 85]. However, these models, based on a constant initiation rate, are not easily applicable to thermo-oxidation. 1985-2000 were essentially marked by the emergence of heterogeneous kinetic models [CEL 93a; GUG 96]. Conventional homogeneous kinetics, however, did not abandon the study of oxidative ageing. Tobolsky's models were rediscovered (Audouin *et al.*, [AUD 95]), then supplemented and coupled with oxygen diffusion, with a numerical resolution of the kinetic scheme (Rincon-Rubio *et al.* [RIN 01]). The use of the numerical tool enabled researchers to do away with almost all the simplifying hypotheses which had, up until then, greatly impaired the credibility of the models, and to reconstruct the kinetic curves, for a rigorous validation in comparison to experimental curves.

Half a century later, we can see how the discipline's evolution is far from having been a long, calm river; we can see inexplicable delays due to missed opportunities: in the western world, Semenov's seminal works only began being used ten years after their publication. Tobolsky's kinetic models remained in obscurity for 45 years. The first models of oxidation-diffusion coupling appeared at the start of the 1980s, although the approach existed at least 20 years beforehand. It had been used, e.g. in the case of PET hydrolysis by Golike and Lasoski in 1961. The relative underdevelopment of the discipline is also due to the long-standing endurance of a number of collective illusions. For example: i) the idea that the ageing of polymers is a phenomenon that has its own laws to be discovered regardless of the underlying processes, the mechanisms of which are considered a black box; ii) the idea that accelerated ageing must above all be a reliable simulation of natural ageing, so that there would be a "correlation" between the two kinds of ageing; iii) the idea that ageing is too complex a phenomenon to be kinetically modeled. This view is still widely held. There will be a section of this book devoted to the issue.

Oxidation: a multi-scale, multi-disciplinary problem

The "target" of the chemical process of oxidation is the elementary structural unit, i.e. typically, the monomeric unit or a smaller group of atoms, in other words a subnanometric structural unit. We shall call this structural scale the *molecular scale*. The major conceptual tool here is organic chemistry, particularly radical chemistry. The experimental tools are from organic chemistry, particularly infrared (IR) spectrophotometry and nuclear magnetic resonance (NMR). Structural changes at this scale may lead to an alteration of the electrical or optical properties, but do not, at a realistic conversion ratio, affect mechanical properties. These may, however, be hugely affected by structural changes on larger scales – particularly:

– The *macromolecular scale*, which relates to the size of macromolecules for linear polymers and that of the network meshes for three-dimensional (3D) polymers. The conceptual tool here is macromolecular physical chemistry, and the experimental tools are specific: e.g. viscosimetry and steric exclusion chromatography (SEC) for linear polymers; measures of modulus in the rubbery state, of swelling in solvents, of glass transition temperature (T_g) for 3D polymers.

– The *supramolecular* (or *morphological*) *scale*, which relates to the spatial arrangement of the chains: crystallinity, in particular the sizes of the lamellae, for linear polymers; spatial fluctuations in the crosslink density for 3D polymers; size of the separate domains in the case of immiscible mixtures, etc. Here, the investigative methods are no longer specific to polymers, they are common to all materials: light, X-rays and neutrons scattering, electron microscopy, atomic force microscopy, etc.

– The *macroscopic scale*, which relates essentially to the skin-core structure linked to kinetic control of oxidation by oxygen diffusion. Macroscopic inhomogeneities induced by processing may also arise, related for example to the thermal gradients in the final phase of the processing operation or to fluctuations in the temperature of the machinery. There are a great many methods in cartography and imaging that have spatial resolutions from a fraction of a micron to a fraction of a millimeter, which can be used to study structure gradients in general and the concentration of oxidation products in particular.

Certain properties of very general interest, such as the fracture properties or rheological properties, do not depend strongly on the molecular structure, but are closely linked to the larger scale structure.

Ageing analysis must therefore always take account of the effects of ageing on all these scales. Since they come from different disciplines, the study of ageing is a multidisciplinary activity, which has no doubt slowed down its development. Take for example the case of polypropylene (PP) oxidation: the main problem here is deep embrittlement, which manifests itself even before the products of oxidation have reached measurable concentrations. We can of course approach the matter using empirical methods, by postulating that there is a correlation between this concentration and that mechanical value, but knowing what slight structural change is likely to embrittle the polymer, and understanding why this change (even if only in a thin superficial layer) can catastrophically alter the impact strength, should offer a clearer view of the problem. This leads us for example to introduce concepts of fracture mechanics, a discipline which was not really developed in terms of polymers until the 1980s, long after the chemical aspects of oxidation. Initially considered to be a purely chemical problem, ageing should progressively become an issue for the material sciences.

Ageing: a problem of kinetics

Ageing can be defined as a slow and irreversible evolution in the structure (in the broadest sense of the word) of a material. By a slow evolution, we understand one which cannot be appreciated on a timescale which is compatible with economical constraints. Therefore we have to turn to accelerated ageing testing and a model capable of predicting behavior in natural ageing (in the use conditions) from the results of accelerated ageing. The term "model" still sounds dreadful to a great many practitioners, but is unavoidable. Whenever we study ageing, we use a model. Let us take the most current example, which consists of comparing lifespans in order to circumvent the problem. Samples A and B have a known lifespan and C is to be studied. Suppose that C's lifespan in accelerated ageing is between those of A and B. We conclude from this that C's lifespan in natural ageing will also be between those of A and B. Here, the model (implicit) is as follows: accelerating ageing does not change the hierarchy of lifespans. If authors using this approach were obliged to explicitly formulate their hypotheses, they would doubtless realize how naïve they are. However, as the tradition in this field is non-communication, aberrations such as the above example endure. We therefore propose to systematically explicitize all the hypotheses made, which would undoubtedly be helpful to the users of the models, as it would offer an evaluation of the dangers inherent in using them to predict lifespan.

Content of chapters

Chapter 1 is dedicated to methodological aspects, particularly the philosophy of our approach based on kinetic modeling, with account taken of the multi-scale nature of ageing.

Chapter 2 is devoted to aspects which are common to all oxidation processes, which have been well known for nearly half a century, and have been the subject of many books (e.g. Reich and Stivala [REI 69]; Denisov and Afanas'ev [DEN 05]).

Chapter 3 describes the three basic kinetic schemes, two of which, with constant initiation rate, have been known for a long time. The third is also old (Tobolsky *et al.* [TOB 50]) but had been completely forgotten by the community until it was rediscovered by our team in the 1990s. The fourth corresponds to the maximum degree of complexity beyond which analytical solutions are useless. The next section describes a number of more complex cases, studied by our team, requiring a numerical resolution. In the final section, we attempt to lay the foundations for a rational approach of kinetic analysis which is certainly not ideal, academically, but which we believe offers the highest ratio of model efficiency to cost of investigation, in view of the current lack of knowledge in the field.

Chapter 4 deals with the coupling of oxidation and oxygen diffusion. Following a brief review of the oxygen transport processes in polymers, we examine the means of introducing diffusion into a kinetic model of oxidation.

Chapter 5 looks at stabilization. The aim here is not to reiterate the detailed descriptions of the mechanisms of stabilization and the exhaustive description of the different categories of stabilizers, which have already been the subject of well-known works (e.g. Zweifel [ZWE 01]). We shall focus essentially on kinetic aspects, which are often overlooked in the existing literature. A relatively large section is dedicated to the processes of stabilizer transport in polymers, the main development being that we can now incorporate these processes into kinetic models, whereas previously, migration and chemical stabilization processes were studied separately and never brought together.

Chapter 6 is given over to a recurring concern in the community of experts in the ageing of polymers, which can be summed up in one question: how can the (slow) molecular mobility which characterizes polymers be taken into account in modeling kinetic behavior? We propose two approaches. The first consists of introducing two competing elementary actions into the mechanistic scheme, of which one depends on mobility and the other does not. The second is to incorporate diffusional terms specific to the reactive species into the model's equations. An original modification to Waite's (1958) theory is put forward. In the third section, we return to the debate: low mobility = heterogeneity. In the final section, we use the concepts already introduced to attempt to account for the fact that glassy polymers are generally more stable in terms of thermo-oxidation than rubbery polymers.

Chapter 7 looks into structural changes caused by oxidation, distinguishing the molecular, macromolecular and morphological scales. The existing literature is very rich in terms of these aspects. Our focus here shall also be on the possible connections between the values which characterize the structure on these three scales and a kinetic model.

Chapter 8 examines the effects of oxidation on physical and mechanical properties. Our goal here is to establish a link – quantitative if possible – between the chemistry of oxidative ageing and material science, to achieve a rational use of the properties in the study of ageing, but above all to approach lifetime prediction with end-of-life criteria which are pertinent from the user's point of view.

Chapter 9 focuses on couplings, and attempts to partially answer the following questions: oxidation generates a state of stress in thick samples. What is the mechanism for this? What are the consequences? When a crack develops, what is the effect of oxidation on its propagation rate? Can a state of stress influence the kinetics of oxidation? Can oxidation influence the kinetics of fracture of a sample

under stress? The fourth section is dedicated to the study of the combination of oxidation and physical ageing by structural relaxation. It seemed important to include a passage in this book about oxidation in processing conditions and its potential impact on recycling. This is the subject of the final section, although here, it must be recognized that the "coupling" aspect is not crucial.

Chapter 10 is a brief overview of oxidation problems caused by irradiation, whether for photochemical or radiochemical processes. Each of these processes merits an entire book in itself, but our approach, as in the previous chapters, is to focus on kinetic aspects. The reader is referred to the abundant literature on the subjects for detailed information about such-and-such a case. The aim here is only to show the extent of the possibilities of kinetic modeling in these areas, particularly photochemistry, where it has been almost completely overlooked. "Natural" ageing, which is very important on the practical level, is the subject of the final section. We do not claim to provide the definitive solution to this complex problem, but rather to indicate the promising paths and those to be avoided.