



Review article

Review of polymer oxidation and its relationship with materials performance and lifetime prediction



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ABSTRACT

All polymers are intrinsically susceptible to oxidation, which is the underlying process for thermally driven materials degradation and of concern in various applications. There are many approaches for predicting oxidative polymer degradation. Aging studies usually are meant to accelerate oxidation chemistry for predictive purposes. Kinetic models attempt to describe reaction mechanisms and derive rate constants, whereas rapid qualification tests should provide confidence for extended performance during application, and similarly TGA tests are meant to provide rapid guidance for thermal degradation features. What are the underlying commonalities or diverging trends and complications when we approach thermo-oxidative aging of polymers in such different ways? This review presents a brief status report on the important aspects of polymer oxidation and focuses on the complexity of thermally accelerated polymer aging phenomena. Thermal aging and lifetime prediction, the importance of DLO, property correlations, kinetic models, TGA approaches, and a framework for predictive aging models are briefly discussed. An overall perspective is provided showing the challenges associated with our understanding of polymer oxidation as it relates to lifetime prediction requirements.

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1. Introduction

Long-term thermo-oxidative degradation is a concern for any polymer under normal environmental conditions, unless sealed systems or purposely introduced inert conditions apply. Therefore, a focal point in the field of 'Polymer Degradation and Stability' is thermally driven degradation. The other big field of course is UV induced photo-oxidation or radiation degradation, where much overlap with thermal aging exists when the effects of temperature on degradation processes are considered. Understanding thermal aging processes, oxidation mechanisms, thermal acceleration behavior, activation energies, and the convoluted manner in which degradation pathways may present themselves, is an integral requirement of meaningful polymer aging studies.

The different methods that are used to evaluate thermo-oxidation may often yield diverging perspectives. It is not always clear if or to what degree extrapolations have predictive value or what complications could be introduced by raising the temperature. Polymer oxidation depends on simultaneous chemical and physical phenomena and accelerative conditions add complexity to this relationship. This overview perspective is therefore intended to

briefly highlight the evolving knowledge with regard to some important aspects when we deal with thermo-oxidative degradation. This also warrants some questions about the assumptions and expected behavior which feed into predictive aging approaches. Some of these challenges are: Can degradation chemistry be simply accelerated? Under which conditions do accelerated aging experiments lose their predictive value? How important are diffusion limited oxidation (DLO) complications? Can kinetic modeling provide predictive capabilities, and if so, where are the limits? What are the ongoing issues that need to be addressed to enable this research field to move forward?

Therefore, to address such questions we will briefly review how thermo-oxidative processes relate to different aspects of polymer chemistry and physics. Further, we will discuss how reaction chemistry has been correlated with mechanical property or molecular weight changes. It is also important to consider the limits of kinetic models or the circumstances under which diffusion limited oxidation (DLO) conditions affect accelerated aging experiments. This opens up a discussion about non-correlations between accelerated and ambient aging conditions. A questionable approach, for example, is the overexposure of polymers in fast thermo-gravimetric analysis (TGA) degradation methods, which in the literature unfortunately may be regarded as a quick substitute for more extended polymer aging studies. We hope to provide a few comments about other intriguing developments and a perspective on how evolving

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material characterization approaches could aid more sophisticated spatially resolved degradation models in the future.

2. Discussion

2.1. Thermal polymer degradation and lifetime prediction

Temperature coupled with oxygen is the most commonly used accelerative condition for polymer degradation as it is easy to apply. It is also an integral part of most other exposure conditions (i.e. photo-oxidation), as is schematically shown in Fig. 1. Materials which do not ‘age well’ are commonly exposed to hotter temperatures until they may ‘fall apart.’ The best example for this approach is given by ramped temperature TGA, since TGA will not ‘fail’ to induce thermal decomposition of organic polymers. In more commonly used accelerated aging studies, temperature and time are perhaps selected based on project constraints, funding availability or even the need to have Ph.D. students publish within a three year timeframe. Whatever the reason, temperature is used for a common purpose, namely to accelerate the underlying ‘degradation chemistry.’ But is it sensible to use accelerated chemistry from a TGA experiment to provide guidance for long term performance of polymers under ambient conditions? It is clear that limits in acceleration factors need to be considered if the resulting accelerated degradation pathways are to be representative.

There are many indications that chemical processes which govern polymer oxidation often follow the ‘holy grail’ of kinetics, which is Arrhenius behavior, as long as moderate conditions and perhaps limited temperature intervals are applied. But significant evidence has also been collected when larger temperature regimes are examined, that many materials show curvature in an Arrhenius plot of oxidation rates [1]. Oxidation rates measured over a large temperature range are an excellent indicator for the relative importance of oxidative processes with temperature and underlying activation energies [1–7]. Textbook chemistry does not always apply and reaction kinetics competes with other processes which induce non-linearity. A schematic of deviations from linear Arrhenius behavior over a large temperature range due to mechanistic changes and DLO is shown in Fig. 2. It shows an Arrhenius plot of relative degradation rate data, which are often called shift factors when obtained from a time–temperature aging data superposition analysis and may be normalized to a particular temperature. Shift factors are proportional to rate and inversely proportional to aging time for a particular aging state. It is common to observe linear Arrhenius behavior over a limited temperature range, but non-linearity may evolve when a larger temperature range is examined due to mechanistic variations in the aging process. The challenges

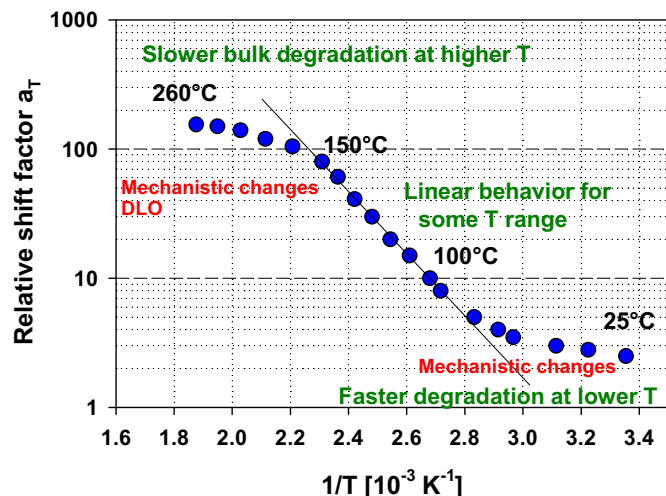


Fig. 2. Most accelerated aging studies use some convenient temperature range where linear Arrhenius behavior may be observed over a limited temperature range. However, non-linearity may be seen when a larger temperature range is examined.

associated with mechanistic changes in dominant chemistry over a large temperature range are at the core of accelerated aging and lifetime predictions [1,5,6,8]. It is therefore imperative that for any accelerated thermal aging study all relevant parallel processes be considered which could add complexity to the analysis of degradation rates and definition of mechanistic reaction schemes. Such issues are evident when dealing with DLO behavior and surface versus bulk degradation phenomena [9–14], heterogeneous versus homogenous aging processes [15–23], liquid state versus solid state kinetic frameworks [19,24,25], or complex TGA signatures [26]; all which affect the interpretation of thermal polymer oxidation.

Thermo-oxidative aging and lifetime prediction are also intrinsically linked with the action mechanism and behavior of polymer stabilizers or additives. Much emphasis of applied polymer testing and aging studies relates to the effectiveness of additives or combinations thereof. It is not the intention of this review to go into details here, since sufficient knowledge and excellent overview literature in this area exists [27–31]. Further, the concerns associated with evaluating stabilizers when using short term high temperature or similar exposure have been discussed before [20,21,32–34]. Correlations between high temperature and low temperature action of stabilizers can be non-existent, because crossover effects exist which project the opposite rating from highly accelerated tests than observed at slower aging conditions [32–34]. The challenges of truly understanding stabilizer performance and their behavior under accelerated conditions are very similar to the examination of materials for lifetime prediction purposes. It is also important to remember that thermo-oxidative degradation will proceed despite the presence of antioxidants. Obviously rates will be much lower for stabilized materials, but significant degradation can occur even when high levels of antioxidant are present [35], or when oxidation induction time (OIT) data may suggest a sufficiently stabilized material [36]. In such situations significant material degradation at lower temperatures is not necessarily inhibited until all antioxidant is consumed, which suggests the participation of localized non-inhibited reaction zones [17,24,35].

2.2. Correlation of degradation chemistry and mechanical properties

Materials performance is usually associated with expected mechanical properties or similar desired attributes (elasticity,

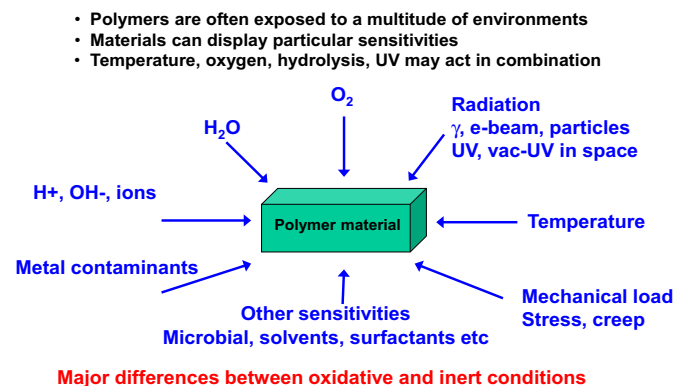


Fig. 1. Various exposure conditions result in polymer degradation where oxygen and temperature are important aging parameters.

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