Degradation Models of High Performance Polymers

Abstract

A review of methods and techniques used to predict the properties of: poly(aryletherketone)s (PAEKs), bismaleimide resisns (BMIs) and poly(etherimide) PEI as high performance polymers over time. These polymers, chosen for their resistance to high temperatures and pressures along with chemical inertness have found use in specialised areas of the oil and gas, automotive, aeronautical and healthcare industries. Understanding how these polymers degrade over time can have a big impact on their usefulness and long term cost.

1. Introduction
2. Modelling and Analysis
   1. Standard Arrhenius modelling of degradation (Control/current standard)
   2. Based on known/identified chemical mechanisms, used DFT/other computational methods to calculated activation energies / rates
      1. Limitations on size of molecules used
      2. Requires knowledge of specific reactions
      3. Combine values calculated for most impactful reactions to obtain an ‘overall’ degradation value and compare to accelerated data.
      4. Calculate against initial repeat unit and modified (degraded) repeat units
   3. Stochastic simulation of using rate of Chain Scission and Crosslinking which could inform prediction of mechanical properties.
      1. Prediction of free volume from these simulations 🡪 Permeability
      2. Existing models?
3. Experimental
   1. Degradation Conditions
      1. Thermal
      2. Thermo-oxidative
      3. Hot/Wet
      4. H2S
      5. Hydrocarbon
      6. Accelerated degradation (TGA)
         1. Separation of chemical degradation and thermal degradation
         2. Ramping and isothermal TGA experiments
         3. Quantification of Diffusion Limited Oxidation processes
      7. Real-time degradation
         1. Temperature points at maximum use temperature and normal use temperature
4. Analysis
   1. Chemical Analysis - Identify specific chemical reactions and their mechanisms under the environmental conditions
      1. Solid state NMR
      2. FTIR
      3. EPR
      4. XPS
   2. Morphology / Tertiary structure Measurements
      1. XRD
      2. DSC
      3. GPC
   3. Predictive Measurements
      1. Permeability measurements
      2. SEM / Optical Microscopy
         1. Track the formation of ‘micro cracks’ which may also impact permeability
5. Extension
   1. Comparison to samples from the field
   2. Additional computational models based on access to higher computing power
      1. Refinement of stochastic models
   3. Model permeability of novel penetrants
6. Conclusions

# Introduction

High performance polymers have found widespread use over the last 50 years, frequently as a replacement for metals in existing technologies. In such applications, these polymers offer reduced weight while offering similar or improved mechanical properties and often strong chemical resistance. While their use is increasing, especially within the aerospace industry, the high cost and manufacturing difficulties associated with them has hampered further adoption.

There is no clear definition of what constitutes a ‘high performance’ polymer, as it is dependent on the application. However, commonly this category of materials has high long term durability at elevated temperatures (177oC, 10,000h) without significant loss of its mechanical properties and can withstand temperatures up to 450oC without experiencing rapid thermal decomposition. Such properties are achieved through a combination of chemical bonding forces and their structure frequently includes: high primary bond strength, a rigid aromatic backbone and, significant secondary bonding. For many commercially produced polymers, different grades are available based on the molecular weight achieved during synthesis. Lower molecular weights are used for improved processability while the highest molecular weight material has improved thermal resistance.

[Diagram of Commercially available performance polymers]

Both thermoset and thermoplastic polymers find their most common application in the formation of composite materials. The addition of glass or carbon fibre to the polymer matrix the mechanical properties of the resulting material are improved. There is a significant body of work dealing with the manufacture, use and degradation of these composite materials.

Long term use of these materials requires an understanding of how relevant properties change over the desired lifetime. The rate and mechanisms of degradation for a material vary heavily depending on the material and environment to which it is exposed.

[Document layout and logic.]

Mathematical modelling of these polymer systems can better our understanding of their behaviour and lifetimes under a wide range of conditions. Current predictive models widely used in industry use many simplifications to make calculations and experiments easier, cheaper and faster. However, through this simplification accuracy is sacrificed which, for the large extrapolations required, limits the effective predictive power of these models. Lifetime prediction relies on the extrapolation of accelerated degradation studies to predict the point at which the measured variable drops below acceptable limits. The chosen variable depends on the application under consideration for the polymer. Typically, for HTHP polymers, this is some mechanical property e.g. Elongation at break.

# Degradation and its measurement

The degradation of a polymer can be caused by chemical, physical or mechanical environmental stresses.

Chemical degradation involves any structural modification to the polymer’s backbone. This is the focus of most investigation, as the macroscale properties of the material are controlled by changes in the chemical structure.

The diffusion of chemical agents into the polymer can be a controlling factor in the rate of degradation. For many polymers, the diffusion of water into the sample is a good predictor of degradation due to hydrolysis.

Physical degradation can cause changes in the mechanical properties of the polymer. Clearly this can become a concern in environments where the material could be cycled above and below the Tg frequently.

Mechanical ageing occurs through the loads and stresses applied to the material in use. This may occur secondary to chemical or physical ageing as the weakened material is no longer able to properly handle the mechanical stresses in its use case.

There is little work in understanding how different mechanisms of degradation affect each other.

# PEEK

# Thermal Degradation

# UV Degradation