Describing Polymeric Degradation Using Simplified Experimental Measurements

Lloyd Smith
Ramachandran Mahadevan

School of Mechanical and Materials Engineering

SAMPE, 37th ISTC
Introduction

• Motivation
  ▪ Degradation of polymers is complex
  ▪ Durability of bonded structures
  ▪ Biomedical applications design for degradation

• Approach
  ▪ Describe degradation using fundamental mechanisms
  ▪ Quantify degradation from simple measurements
  ▪ Compare thickness effects
Degradation Mechanisms

- Surface erosion

- Bulk erosion
Environmental Exposure Facility

- Aggressive environments
- Temperature
- Stress
- Time
Environmental Exposure Facility
Measuring Degradation

- Weight Change
- Thermal response (Differential Scaling Calorimetry)
- Dynamic Mechanical Analysis (DMA)
- Dielectric Analysis (DEA)
- Molecular mass change (Gel permeation chromatography)
- Photo degradation (activation spectrum)
- Structural changes (SEM)
Observed Weight Changes
Modeling Degradation

- Empirical models
- Mechanistic models
- Numerical models
  - Monte-Carlo
  - Finite element analysis
Proposed Model

• Approach
  ▪ Diffusion (Fick’s Law)
  ▪ Chemical reaction

• Assumptions
  ▪ Through thickness effects (1-D)
  ▪ Bulk degradation (constant volume)
  ▪ Constant diffusion constant
  ▪ Constant reaction rate constant
Diffusion Effects (Fick’s Law)

\[ C(t, z) = C_0 \cdot \left[ 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \left( \frac{1}{2j+1} \right) \sin \left( \frac{(2j+1) \cdot \pi \cdot z}{h} \right) \exp \left[ -\frac{(2j+1)^2 \cdot \pi^2 \cdot D \cdot t}{h^2} \right] \right] \]
Chemical Reaction

• Reaction kinetics

\[ \frac{dC}{dt} = kC^n \]

• Solve using:
  - First order (n=1)
  - At t=0, C=C_0

\[ C(t) = C_0 e^{-kt} \]
Modeling Degradation

\[-\frac{d[C]}{dt} = k[C]\]
\[\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial z^2}\]

\[C(t, z) = \int_0^t C_0 e^{-k(t-\tau)} \cdot \left[\frac{dC}{d\tau}\right] \cdot d\tau\]

\[\overline{C}(t) = \frac{1}{h} \int_0^h C(t, z) \cdot dz\]
Model Parameters

• Measure directly
  ▪ Thickness (h)

• Measure indirectly
  ▪ Diffusion coefficient (D)
  ▪ Saturation concentration (C_o)
  ▪ Reaction rate constant (k)
Parametric Study

- Concentration vs. square root of time for different values of $K$.
- Concentration vs. time for different values of $D$.
- Concentration vs. time for different values of $h$.
Experiments

• Material
  ▪ Aquazol (Poly(2-ethyl-2-oxazoline))
  ▪ water soluble polymer

• Process
  ▪ 2 in. by 2in.
  ▪ 0.13, 0.16, 0.20 in. thick
  ▪ 5 psi, 60 min @ 350F
Measuring Degradation

- Dry coupon (200F, 24 hrs)
- Measure coupon volume (V)
- Calculate solvent saturated coupon weight
  \[ W_{sat} = \rho_{H_2O} V \]
- Immerse coupon in H_{2}O for controlled durations
- Weigh wet coupon (W_{w})
- Dry coupon, weigh again (W_{D})
- Calculate solvent concentration
  \[ C(t) = \frac{W_{w} - W_{D}}{W_{sat}} \]
Determining Coefficients

• Fit to all data (three thicknesses)
• Fit to one data set
  ▪ Compare with other thicknesses
Comparison of predicted and measured moisture concentration
Parameter Comparison

![Graph showing concentration and saturation level against time and thickness.](image-url)
Summary

• A model polymer was identified to study degradation

• The effects of degradation and diffusion can be separated from weight measurements

• Classical descriptions of diffusion and chemical reaction can describe diffusion controlled degradation