Accelerated Aging Studies
and the
Prediction of the Archival Lifetime
of
Optical Disc Media

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Outline:

- Optical Recording
- Failure
- Some Data
- What is Accelerated Aging
- The Science of Accelerated Aging
- Sample Analysis Methods
- What is Needed
Optical Recording Primer

**DVD-R**

- Au reflective layer
- Dyed-polymer layer
- Polycarbonate substrate thickness = 0.6 mm

**DVD-RW**

- Dielectric layer
- Phase-change alloy
- Dielectric layer
- Polycarbonate substrate thickness = 0.6 mm
Optical Disk Substrate Materials

Polycarbonate

- Dominant substrate material
- $T_g = 150^\circ C$

Polycyclohexylethylene

- Dow Chemical
- $T_g = 146$ to $150^\circ C$
- Low birefringence

Topas®

- Ticona
- Random copolymer of ethylene and norbornene
- $T_g = 70$ to $225^\circ C$
- Low birefringence
Dyes Used in CD-R Disks

Cyanine Dyes

Nickel Bisdithiolate Complexes
stabilizer for cyanine dyes

Naphthalocyanines
Phase Change Alloys

Ge Te Sb Ag In Co Se Au Bi As
Failure

- All materials fail!
- Acceptable vs. Catastrophic Failure
- How will it happen?
- How long will it last?
- Do we care?
Physical Failure

- Polymer embrittlement
- Layer de-adhesion
- Birefringence from free volume consolidation
- others….
Chemical Failure

**DVD-R**
- Expect the dye to be the weak link
- Photochemical degradation
- Reaction with moisture and oxygen (slow — reaction kinetics limited)
- Reaction with ozone (fast — mass transfer limited)

**DVD-RW**
- Corrosion of the phase change alloy
- Requires diffusion of oxygen and water through the polycarbonate, through pinholes in the dielectric layers
- Probably Mass transfer limited
Accelerating Aging Studies

Expose disks to high temperature and high humidity conditions

- 65°C and 80% relative humidity
- 80°C and 80% relative humidity
- 90°C and 90% relative humidity

Measure the carrier to noise ratio (CNR)

- 830 nm laser diode
- Record at 2.5 MHz carrier frequency
- Media velocity 5.65 m/s
- Read power 0.5 mW
- CNR in a 30 kHz bandwidth

Accelerated Aging Studies at 80°C and 80% Relative Humidity
Disks Exposed to 80°C and 80% Relative Humidity

![Graph showing CNR (dB) vs Exposure Time (hours) for different HCC Disks.](image-url)
Disks Exposed to 65°C and 80% Relative Humidity

CNR (dB) vs Exposure Time (hours)

- HCC Disk #5
- HCC Disk #6

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Disks Exposed to 90°C and 80% Relative Humidity

**Diagram:**

- **Y-axis:** CNR (dB)
- **X-axis:** Exposure Time (hours)
- **Graph Title:** HCC Disk #7

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Accelerated Aging

Can we change the environmental conditions to which a material is exposed and increase the rate at which degradation and/or failure occurs?

For example, elevated exposure to light, heat, or chemical ‘bad actors.’

Can we do it in such a way that the results make sense? are useful? are predictive?
Material Clocks

Effect of Temperature:
A Gedanken Experiment
Material Clocks

How do we quantify this?

\[
dt^* = \frac{dt}{a_X[X(t)]}
\]

\[
a_X = \frac{\lambda(X)}{\lambda(X_0)}
\]

\[\lambda = \text{relaxation time}\]

\[X = \{T, c, \tau, RH, \ldots\}\]
Problems with Material Clocks

• Uniform X dependence of relaxation modes
• Phase transitions
• Determining $\lambda(X)$
• Multiple X’s
Reactive Mass Transfer:

Conservation Relations

\[
\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i - R_i
\]

\(R_i = \) rate of destruction of species \(i\) by reactions

\(J_i = \) mole flux of species \(i\)

\[
J_i = -D_{ij} \nabla c_j
\]
A Simple Example

\[ \text{polymer overcoat} \]

\[ \text{dye + polymer} \]

\[ A + \text{Dye} \rightarrow \text{Products} \]
Assumptions

- Steady State
- One Dimensional Diffusion
- Effective Binary System: single penetrant with stationary substrate
- Fickian Diffusion
- Single Degradation Reaction
- Polymer Does Not Degrade
- Degradation Reaction Occurs at Interface
Kinetically Limited Case

Mass Transfer Rate >> Reaction Rate

Rate of Degradation = Rate of Reaction

Assume Arrhenius Temperature Dependence of Reaction Rate: \( R_A \propto e^{-E_r/T} \)

Then:

\[
R(c, T) = R(c_o, T_o) \left[ \frac{c}{c_o} \right]^n \exp \left[ E_r \left( \frac{1}{T} - \frac{1}{T_o} \right) \right]
\]
Mass Transfer Limited Case

Reaction Rate >> Mass Transfer Rate

Rate of Degradation = Rate of Penetrant Arrival at Interface

\[ \frac{-D_{AM}}{\delta} \ln(1 - x_{As}) \]

Assume: \[ D_{AM} \propto e^{-E_d/T} \]

Then:

\[ R(T,x_{As}) = R(T_o,x_{Aso}) \left[ \frac{\ln(1-x_{As})}{\ln(1-x_{Aso})} \exp \left[ E_d \left| \frac{1}{T_o} - \frac{1}{T} \right| \right] \right] \]
Reactive Mass Transfer:

Conservation Relations

\[ \frac{\partial c_i}{\partial t} = -\nabla \cdot J_i - R_i \]

\( R_i = \) rate of destruction of species i by reactions

\( J_i = \) mole flux of species i

\[ J_i = -D_{ij} \nabla c_j \]
Assume first order kinetics: $R_A = -kc_A$

Then (as per Danckwerts):

$$c_A(r,t) = e^{kt}c_A^d(r,t) - k \int_0^t e^{kt'}c_A^d(r,t')dt'$$

Where $c_A^d(r,t)$ is the solution in the absence of reaction.
A material clock?

Let:

\[ ds = \frac{D_{AM}(T)}{D_{AM}(T_0)} dt \]

Assume:

\[ k(T) = k_o \exp \left[ E_r \left| \frac{1}{T_0} - \frac{1}{T} \right| \right] \]

Then:

\[ c_A^d(r,t,T) = c_A^d(r,s,T_0) \]

A material clock!
But:

\[ c_A(r, t, T) = e^{k_0 \left\{ \exp \left[ E_r \left| \frac{1}{T_0} - \frac{1}{T} \right| \right] t \right\} c_A^d(r, s, T_0)} \]

\[ -k_0 \left\{ \exp \left[ E_r \left| \frac{1}{T_0} - \frac{1}{T} \right| \right] \right\} \int_0^t \left( e^{k_0 \left\{ \exp \left[ E_r \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] t' \right\} c_A^d(r, s', T_0)} \right) dt' \]
Problems with Assumptions

- Multiple (many) species / Multiple (many) reactions
- Neither mass transfer nor diffusion limited
- Thermophysical properties vary with time
- Reaction products promote further degradation
- Mass transfer in polymers is not Fickian

and...
Polycarbonate Degradation

The ester linkages in polycarbonate are susceptible to hydrolysis.

The activation energy for hydrolysis was $70 \pm 4$ kJ/mol.

Conclusions

The materials package is sufficiently complicated that a rational basis must be devised for accelerated aging.

Is it possible to find a suitable ‘material clock’?

Must identify the fundamental mechanisms of failure.

Require kinetic data (reaction and transport) for failure mechanisms.

There is a lot of work that could/should be done on this problem!