Analysis of the Transient Behavior of Biopolymers with DSC and Rheology

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Outline

- Background of Total Hip Replacement (THR) Surgery
- Materials and Issues
  - Polyethylene
  - Acrylic bone cement
  - Analytical techniques
- Analysis of bone cement
  - DSC
  - Rheometry

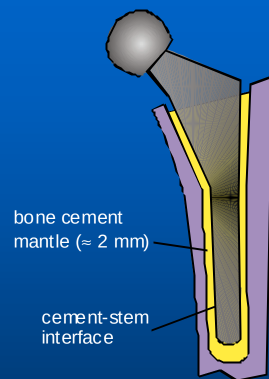
History of THR

- Charnley (1962)
- 258,000 THR in US (1994)
- 620,000 THR &TKR WW (1997)
- Average cost: $51,000
- Total: $13 billion in US alone
- 7 Orthopedic Manufacturers

THR Materials

- Femoral Head
  - Stainless steel
  - ceramic
  - cobalt chrome
- Stem
  - ss, CoCr, composite
- Acetabular Liner
  - UHWMPE
  - ceramic
  - stainless steel

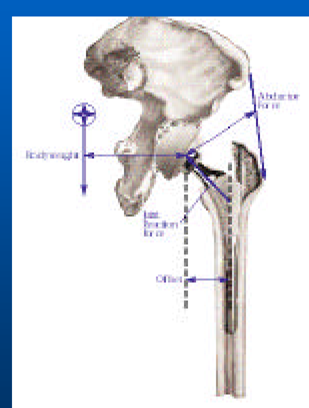
Cemented vs. Cementless Implants



•50% of THR use cemented stems
•Used primarily in older patients

Issues in Long-Term Stability

- Lysis (resorption of tissue)
- Septic Loosening
- Aseptic Loosening
- Characterized by:
  – Thigh pain
  – Hip pain



Sources of Osteolysis

- Wear debris generated from bearing surface
- Debris from bone cement
- Chemical and thermal necrosis
- <9% of patients require revision surgery

Advances in THR

- Septic loosening (infection)
  - clean room environment
- Improvements in surgical instruments
  - alignment of components
- Revision surgery technique improved
- Acetabular Liner Material

Acetabular Liner

- Ultrahigh molecular weight polyethylene (UHMWPE)
- Good properties
  - creep
  - modulus
  - compression strength
  - biologically inert
- Adequate properties
  - wear

Improve this without degrading good properties

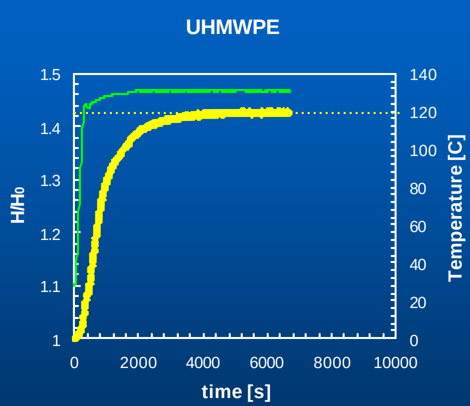
Crosslinking UHMWPE

- Results in improved wear behavior
  - less molecular orientation
- Some reduction in crystallinity
  - decrease in mechanical properties
- Introduces free radicals
  - reacts with oxygen
  - results in long-term embrittlement

Analytical Techniques

- Wear studies
  - Hip simulator, pin-on-disk
- Oxidation index, trans-vinyl index
  - micro FTIR
- Degree of crosslinking
  - Swelling studies

Swell Ratio Tester (SRT-1)



- **crosslink density**
- **molecular weight between links**

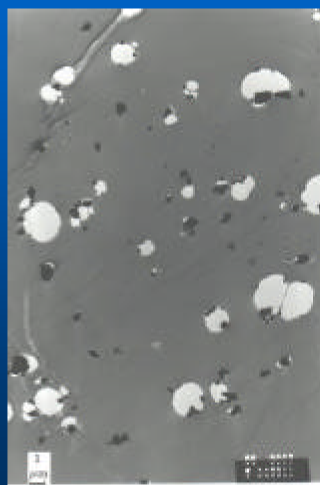
Other Issues

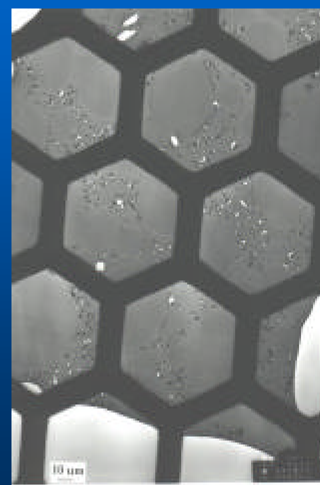
- Bone Cement
  - Particle generation
  - Aseptic loosening
  - Thermal necrosis
  - Chemical necrosis
  - Mechanical properties

Composition of Bone Cement

Powder		**Liquid**	
PMMA	15 wt%	MMA	97 vol%
PMMA co-PS	74 wt%	N,N-dimethyl-p-toluidine	2.6 vol%
Barium Sulfate	10 wt%	Hydroquinone	75 ppm
Benzoyl Peroxide	1 wt.%		

Bone Cement





Variations in Bone Cement

- Additives
  - fibers
  - tricalcium phosphate, hydroxyapatite
  - carbon particles
- Initiator percentage
- Accelerator

Kinetics of Reaction

- Free radical polymerization

disassociation	$I \xrightarrow{k_d} 2R\bullet$
initiation	$R\bullet + M \xrightarrow{k_i} RM\bullet$
propagation	$RM_n\bullet + M \xrightarrow{k_p} RM_{n+1}\bullet$
termination	$RM_n\bullet + RM_m\bullet \xrightarrow{k_t} RM_{m+n}$

Kinetics (continued)

Primary radical production

Rate of polymerization

$$R_d = 2fk_d[I]$$

$$R_p = k_p(fk_d[I]/k_t)^{1/2}[M]$$

$$= k[M]$$

Assumes a steady state free radical concentration

Monitoring reaction

- FTIR (Rehman et al., 1996)
  - examine concentration of double bonds in monomer
- X-ray, mechanical
  - kill reaction at various times and test
- DSC
- Rheometry

Differential Scanning Calorimetry

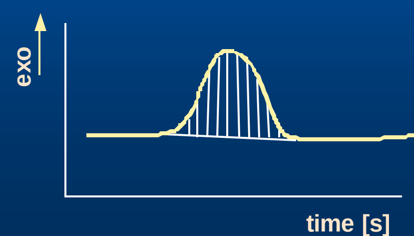
- Isothermal tests
  - measure heat generation vs. time
- Calculate
  - extent of reaction
  - rate of reaction
  - kinetics of reaction
  - residual monomer

Procedure

Maintain equal temperatures

Mix powder and liquid

Measure heat flow Q(t)



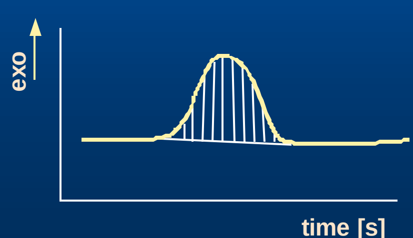
Extent of Reaction

$$a = \frac{Q(t)}{Q_{tot}}$$

$$a_{\max} = c + dT$$

Q_{tot}: determined from scanning experiments to ensure all monomer has reacted.

The extent of reaction will depend on the test temperature.



Extent of Reaction

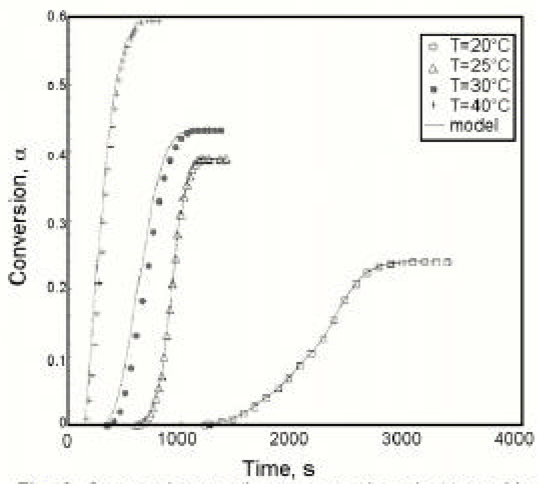


Fig. 6. Conversion vs. time: comparison between kinetic model predictions and experimental data at several temperatures in isothermal conditions.

- Different induction times
- Different final conversions
- Different kinetics

Nzihou et al, 1999

Induction Time

- Characteristic of the inhibitor-initiation reaction

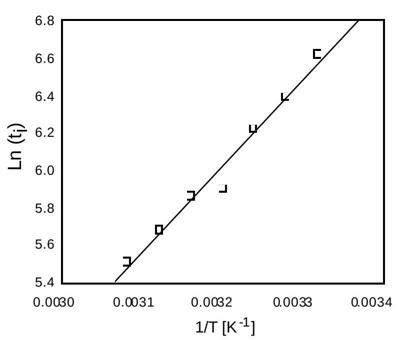


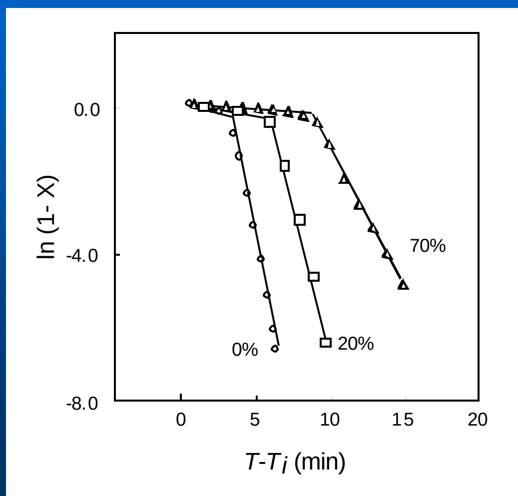
Fig. 3: Isothermal induction time vs. temperature

$$t_i = \frac{1}{K\exp(-\frac{E}{RT})}$$

E=71.4 kJ/mole

Nzihou et al, 1999

Propagation Reaction



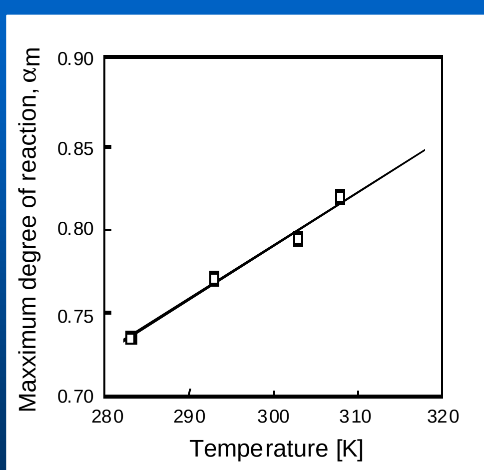
Yang, 1997

- **Effect of tricalcium phosphate**

$$\frac{d[M]}{dt} = -k[M]$$
$$\ln[M/M_0] = -kt$$
$$\ln[1-X] = -kt$$

- **first order kinetics**
- **TCP content affects:**
  - **induction time**
  - **rate constant**

Maximum Conversion



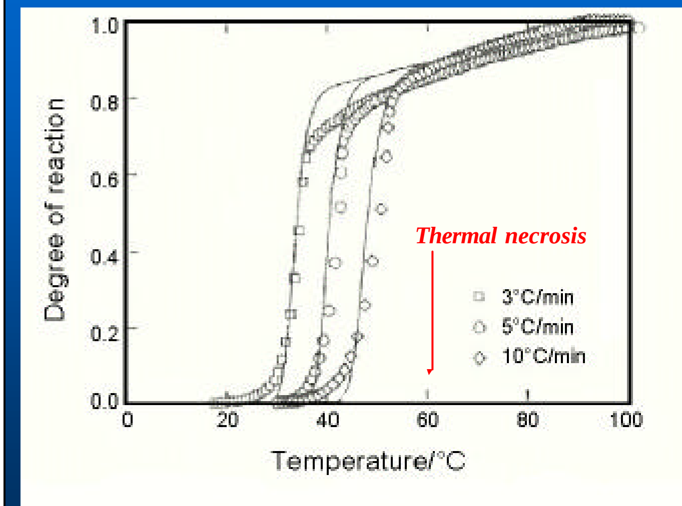
Maffezzoli (1996)

$$a_{max} = c + dT$$

- **Diffusion of monomer is limited as viscosity increases**
- a_m **approaches 1 as** $T \to T_g$

- **T_g = 105 C**
- **T_b (MMA)= 100 C**

Non-isothermal Experiments



- **Maximum conversion goes to 1**
- **Heat evolution and test temperature are both changing with time**

Maffezzoli (1996)

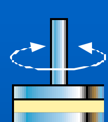
Rheology

- Typically performed on materials with unchanging parameters
  - measure f(shear rate, frequency, temperature, stress)
- Researchers applying rheology to 'mutating' materials
  - curing polymers (epoxies)
  - evaporating solvents
  - degradation

Rheology and Bone Cement

- Used to characterize cement handling behavior as a function of cure time
- Steady shear experiments
  - Ferracane amd Greener (1981)
  - Farrar and Rose (1998)
  - Nzihou et al (1998)
- Problem: steady shearing will increase free radical migration
- Does not mimic clinical use

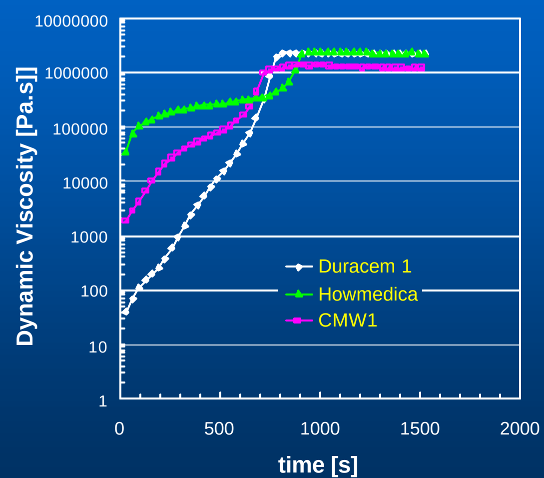
Small Amplitude Oscillatory Testing



- **Cement undergoes moderate deformation**

- **o**btain
  - dynamic viscosity
  - Storage and loss modulus
  - tan δ
  - volumetric shrinkage
  - up to and through cure

Comparison of Bone Cements



Aseptic Loosening of Stems

James et al, 1993

- Extensive interfacial porosity in failed implants
- Crack initiation occurs at pore sites in fatigue study (James, 1992)
- Retrieval study showed failure occurred at cement-stem interface (Jasty, 1991)

Conclusions

- DSC
  - Valuable tool to study the kinetics of curing systems
  - Extent of reaction, rate of reaction, rate constants
- Rheometry
  - Useful to monitor the physical behavior of the curing bone cement

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