

Polymerization Fronts, Mechanical Constraint and Shrinkage Induced Residual Stresses in Bone Cement: A one-dimensional coupled thermal-kinetics-viscoelastic model of in-situ polymerization

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Introduction: In-situ polymerizing biomedical polymers are exposed to multiple, highly complex, coupled phenomena that include temperature-dependent polymerization kinetics, heat generation and transfer, polymerization shrinkage, and local/global mechanical constraint. These factors can interact during polymerization to yield several important, yet poorly understood behaviors, including polymerization fronts and pore formation¹. Polymerization fronts are discrete fronts that move through polymerizing material where ahead of the front the material is substantially unpolymerized, while behind the front it is nearly fully polymerized. The consequences of such fronts in terms of polymerization and development of residual stresses and porosity have not been clearly elucidated. The goal of this study is to present a simplified, 1-D coupled analysis of a polymerizing bone cement in the presence of mechanical constraint. It predicts conversion, temperature, and residual stresses and strains that arise when the overall length of the cement is held fixed.

Methods: The empirical kinetics equations of Li et al. are used², along with the 1-D heat transfer equation with a heat generation term to reflect the heat evolved due to polymerization (56 kJ/mol MMA).

$$\frac{d\alpha}{dt} = k(T)\alpha^n(1-\alpha)^m \quad \frac{\partial T}{\partial t} = \frac{\kappa}{\rho C_p} \frac{\partial^2 T}{\partial x^2} + \frac{\Delta H M_o}{C_p} \frac{\partial \alpha}{\partial t}$$

The temperature (T) and conversion (α) distribution at any time is determined and these are used to find the local reaction rate constant ($k(T) = k_o e^{-Q/RT}$). The 1-D model consists of 100 elements across 6 mm of cement where the ends are held at a fixed temperature. The mechanical model consists of Maxwell viscoelastic elements connected in series (See Fig. 1) and is subjected to overall constraint in its deformation along its length (no net shape change). As the cement polymerizes, it will want to shrink due to polymerization contraction. This shrinkage will vary locally with conversion and, with mechanical constraint, will give rise to tensile residual stresses and strains. The amount each element stretches will depend on that element's mechanical properties which vary with conversion. Empirical equations for the modulus and viscosity as functions of conversion are:

$$E(\alpha) = E_i + (E_u - E_i)\alpha^r \quad \eta(\alpha) = \eta_l + (\eta_u - \eta_l)\alpha^q$$

This interaction between local shrinkage strain, locally changing material properties and series connections of elements is used to predict the residual stress as well as local strains and strain energy. Several computer experiments were conducted. One was where the cement started with a uniform temperature (27 °C), with the left side held at 37 °C, and the right side held at 27 °C. Predictions of T, α , residual stress and local residual strains and strain energy were made versus position and time. All of these coupled equations were solved

numerically using finite difference methods. The model was validated using simple conditions where the result is known and comparing the analysis with these results.

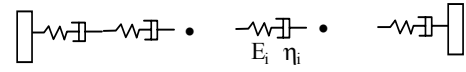


Figure 1: Series Maxwell model of constrained polymerizing cement. The overall length is held fixed as each element shrinks due to local polymerization and property changes.

Results and Discussion: Selected results for the conditions listed above are shown in Figs. 2 and 3. Fig. 2 shows the conversion versus position for different times and Fig. 3 shows the residual strain energy versus position and time. It can be seen that 10 °C temperature differences can give rise discrete polymerization fronts and that these fronts can cause very high localized regions of strain energy (in the unpolymerized region on the Right in Fig 2). This strain energy may be a source of void (pore) nucleation, gap formation or cement fracture.

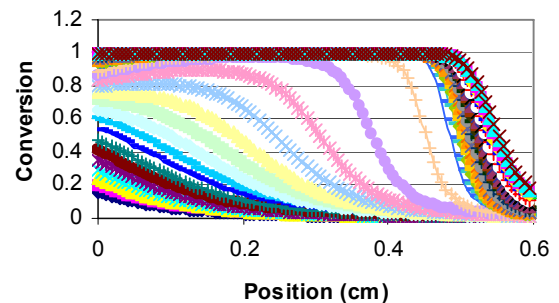


Fig. 2: Conversion profiles showing a polymerization front moving from left to right with time.

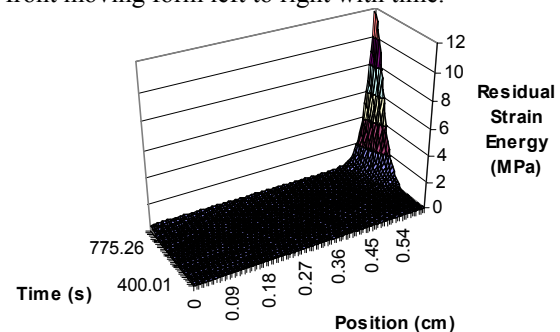


Fig. 3: Strain energy vs x and t: Note high energies present on right in unpolymerized cement. Strains were dependent on conditions and as high as 15 times those of the average strain. Residual stresses up to 70 MPa were observed depending on properties with α .

Conclusions: These results demonstrate that polymerization is highly complex and can give rise to high local residual strain energy and residual stresses. These effects may be a source of void nucleation and may explain interfacial porosity formation and cement fracture. **REF:** 1. Gilbert, JL, JBMR, 2000, 2 Li et al. 2003, Med. Eng. & Phy.