Thermal characterization of PMMA-based bone cement curing

CHAODI LI, JAMES MASON*
Aerospace and Mechanical Engineering Department, University of Notre Dame, Notre Dame, IN 46556-5637, USA
E-mail: mason.12@nd.edu

DON YAKIMICKI
Research Department, Zimmer, Inc., Warsaw, IN 46580, USA

In thermal characterization tests of polymethylmethacrylate bone cement performed according to the *ASTM Standard Specification for Acrylic Bone Cement*, time–temperature profiles of bone cement were observed to be sensitive to the thickness of the cement patty and the mold material. Due to the heat transfer from cement to the surrounding mold, such tests might underestimate the exothermic temperature of bone cement. Developing test methods to better characterize cement thermal behavior is necessary for accurate cement curing simulations. In this paper, the effects of the mold material and geometry on experimental measurements of bone cement setting temperature and setting time were evaluated by conducting the polymerization in different test molds. Finite element (FE) numerical simulations were also performed to provide a further understanding of these effects. It was found that the mold material and geometry significantly influence the values of the parameters measured using the ASTM standard. Results showed that the setting temperature measured was about 50 °C lower in a polytetrafluoroethylene (PTFE) mold than in a polyurethane (PU) foam mold for the 6 mm thickness cement. The measured peak temperature using PTFE molds varied about 75 °C for different mold heights (6 mm vs. 40 mm), but only by 28 °C with PU molds. The measured setting time with PTFE molds varied by about 740 s for different mold heights (6 mm vs. 40 mm), while only by about 130 s for PU molds. Using PU foam materials for the test mold decreases cement heat transfer effects due to the poor heat conductivity of PU foam and provides more consistent measured results. FE parametric studies also support these observations. Poor conductivity materials, like PU foam, make better molds for the characterization of bone cement thermal behavior.

1. Introduction

Bone adjacent to a prosthesis is exposed to heat generated by the polymerization of polymethylmethacrylate (PMMA) bone cement in cemented hip arthroplasties [1–3]. The elevated temperatures in the bone may lead to thermal necrosis of bone, and subsequently induce implant loosening. It has been found that the extent of bone necrosis depends on temperature rise and duration [3–6]. One critical problem associated with performing bone cement thermal investigations is how to accurately characterize bone cement thermal parameters. ASTM standard F-451: *The ASTM Standard Specification for Acrylic Bone Cement* [7] provides the methods for determining bone cement setting temperature and setting time. However, in the thin patty (6 mm) tests described by the ASTM standard, time–temperature profiles of bone cement in the tests were observed to be sensitive to the thickness of the patty and the mold material [8, 9]. Due to heat transfer from cement to the surrounding mold, such tests might underestimate the exothermic temperature of bone cement. Few investigations have been performed to study bone cement heat generation and conduction behavior related to the surrounding mold and to fully characterize such effects. The goal of this study was to better understand how test molds affect the temperature history in the bone cement during thermal characterization experiments. The aim of this paper is to improve the test method for experimental characterization of bone cements used with joint replacements. The effects of the mold materials and the geometry were evaluated by conducting the polymerization of bone cement with different mold designs. The influence of mold material and geometry on the measured thermal parameters of

*Author to whom all correspondence should be addressed.

bone cements was also parametrically investigated by the finite element (FE) numerical method to provide a further understanding of these effects.

2. Materials and methods

2.1. Materials

The material examined was a modified form of Osteobond® without barium sulfate, manufactured by Zimmer, Inc. (Warsaw, Indiana, USA). This bone cement, like many other bone cement systems, is formed by mixing the co-polymer poly(methylmethacrylate)-poly(styrene) solid powder with methylmethacrylate liquid. The experimental bone cement used in this study consisted of a solid phase made of poly(methylmethacrylate)-co-poly(styrene) powder with an average particle diameter of about 50 μm containing 0.8% benzoyl peroxide (BPO). The liquid phase is made of the methylmethacrylate monomer (MMA) with 0.25% dimethyl-p-toluidine (DMPT) as the initiator, stabilized with 50 ppm of hydroquinone inhibitor.

2.2. Experiments

Cylindrical molds (Part A in Fig. 1) with different internal heights ranging from 6 mm to 40 mm (internal diameter: 60 mm) were designed for the evaluation of the peak temperature and setting time of bone cements during curing. A 10 mm thick cover (B) was designed to thermally insulate the tests. Two different materials were selected for the test molds: polytetrafluoroethylene (PTFE) (8545KAC Virgin Electrical Grade Teflon®, http://www.mcmaster.com) and polyurethane (PU) (FR-3702 PU foam, General Plastic Inc, Tacoma, Washington). The PU foam molds were cut from block material and then coated with a thin layer of MS-78 ionomer film (Flex-O-Glass, Chicago, Illinois) using a vacuum thermal forming process. The coating is believed to be nonreactive with bone cement in the test. The thin coating was added to prevent flow of cement into the foam cells. Bone cement thermal tests were performed in a temperature-controlled chamber (D) held at varying temperatures. Thermocouples (Type: TT-J-24, Omega Engineering, Inc., Stamford, CT, USA) were positioned with their junctions (C) in the center of the molds of the internal cavity to measure the temperature during cement curing, as described by the ASTM standard [7].

In the studies of the effects of test mold material and geometry, all equipment and mixing materials were maintained at 23 ± 2 °C for at least 2 h prior to testing and all tests were conducted at 23 ± 2 °C and 50 ± 10% relative humidity. Bone cement goes through three phases during curing: mixing of the solid and liquid, gel formation and polymerization of the monomer [3]. For these experiments, the solid component was placed in a glass beaker and mixed with liquid component for one minute. The mixture was then gently packed into the cylindrical mold until full and the thick cover was immediately pressed down to thermally isolate the cement (Fig. 1). Immediately, the cover was set in place with a C-clamp to produce the desired height of the bone cement specimen. Then, the excess materials and the C-clamp were removed. The temperature was continuously measured with respect to time using a thermocouple placed at the center of the mold.

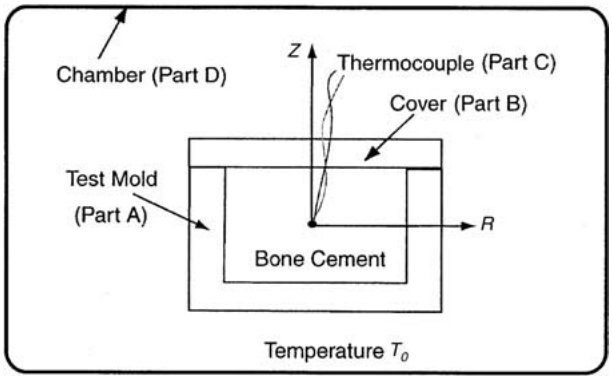

Figure 1 Schematic of thermal test setup.

In this paper, two important bone cement curing parameters were studied: setting temperature and setting time. The setting temperature was taken as the maximum temperature reached during the polymerization reaction. The setting time was taken as the time when the temperature rise was at a point halfway between the maximum temperature and the ambient temperature, as defined by ASTM Standard F451 [7].

2.3. Finite element analysis

In order to provide a better understanding of the tests, parametric finite element studies were performed to investigate the influence of the mold material and geometry on characterization of bone cement. The polymerization kinetics of the bone cement are modeled by the following expression [10, 11]:

$$\frac{\partial \alpha}{\partial t} = Z_0 e^{((E_a)/(RT))} \alpha^m (1-\alpha)^n \qquad (1)$$

where Z_0 is a constant; E_a is the activation energy; R is the universal gas constant; T is the absolute temperature, α is the degree of conversion, and m and n are the reaction order constants. The conversion parameter, α, ranges between zero and one. Typically, the values of Z_0, E_a, n and m must be obtained from experiments. Here, the test results with the internal mold height of 20 mm of PU foam mold were selected as the correct experimental data. Because of the mathematical characteristics of the polymerization kinetic model given by Equation 1, the initial reaction completion parameter α_0 cannot be zero, otherwise no reaction occurs. Due to the difficulty in obtaining the initial value α_0, it is usually arbitrarily selected in the reports in the literature. However, it has been found that the initial value of α_0 significantly affects the predicted rate of reaction, and therefore polymerization setting time [8, 9]. In this research, the parameter was assumed as one of the variables in the optimization operation to best fit the experimental results. Therefore, the method we developed obtains α_0 by matching the predictions to experimental data. Thus, there are five unknown parameters Z_0, E_a, α_0, m and n in the kinetic model. Experimental data was gathered for polymerization at five different values of T_0 ranging between room temperature (23 °C) and human body temperature (37 °C). An optimization parametric study was then

performed to minimize the error between numerical predictions using the kinetic model and the experimental results for various values of T_0 [8, 9]. Thus, we obtain the five unknown parameters. Coupling the cement kinetic model with the energy balance equation, a FE method was developed to simulate bone polymerization heat generation and conduction. The numerical method implementation was described in detail elsewhere [8, 9]. With the input data of the mold material properties and geometry, the initial and boundary conditions of the thermal tests, the numerical method was used to predict the temperature development at the position of the thermocouple. In the simulations, the heights of the mold and mold materials were varied for parametric evaluations of their effects.

3. Results and discussion

The bone cement curing time–temperature curves in experiments following the ASTM Standard F-451, while varying the mold materials, are shown in Fig. 2 (internal height of the mold is 6 mm). The measured setting temperature with the PU foam material mold is about 95 °C, while it is only about 45 °C with the PTFE mold. Also, it is seen that thermal tests with PU molds are more consistent. The setting temperature varies by only 4 °C between the several PU mold tests while compared to tests with a PTFE mold where the setting temperature varies by 11 °C between the different PTFE mold tests. The experimentally measured setting temperature and setting time for the two mold materials and various heights of the molds are shown in Figs. 3 and 4, respectively. As shown in Fig. 3, the setting temperature increases with increasing the mold height. A decrease in the setting time as the mold height increases is shown in Fig. 4. The variations of setting time (1623–2389 s) and

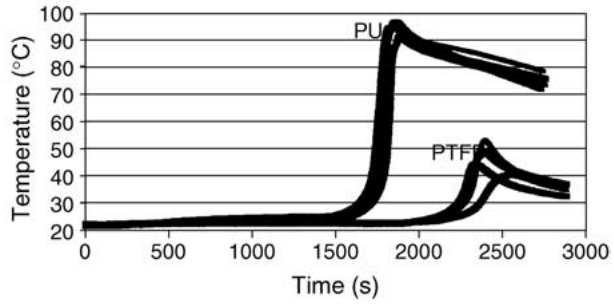

Figure 2 Cement temperature-time history in different material molds (ASTM standard F-451; cement thickness: 6 mm).

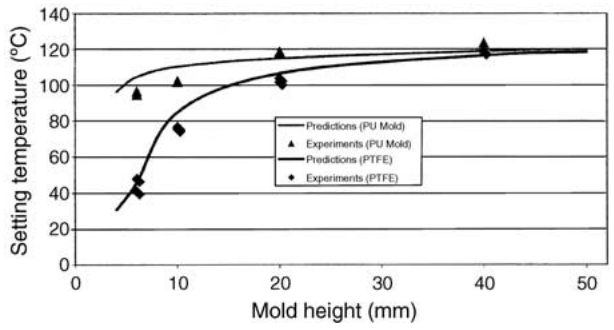

Figure 3 Cement setting temperature in different molds.

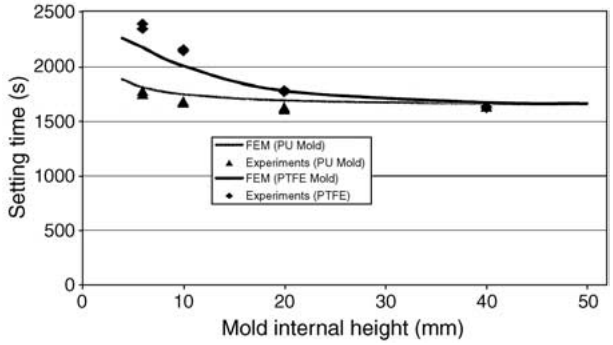

Figure 4 Cement setting time in different molds.

temperature (45–120 °C) using different height (6–40 mm) PFTE molds are larger than those measured using different height PU molds (setting time: 1635–1778 s; setting temperature: 95–123 °C). These results show that the setting temperature during curing not only depends on the total polymerization heat release over a period of time, but also on the heat conducted to the surrounding materials, i.e. test molds. Although the polymerization reactions occur in a very short time (about 200 s) compared to curing time, the effect of the heat release to the mold on the bone cement setting temperature and the setting time is still significant, especially for relatively high conductivity materials. A thicker patty reduced the effects of the thickness variation and mold materials on the characterization parameters of bone cement to a more manageable level. When the mold is sufficiently high, the setting time and temperature with different mold materials converge to a limiting value, independent of mold materials (Figs. 3 and 4).

Results shown in Fig. 2 indicate that the setting temperature measured was about 50 °C lower in the PTFE mold than that in the polyurethane mold for a 6 mm patty thickness. The measured peak temperature with the PTFE molds varies by about 75 °C with different mold heights (6 vs. 40 mm), but only by 28 °C with the PU molds. The measured bone cement setting time with the PTFE molds varied by about 760 s for different mold heights (6 vs. 40 mm), but only by 140 s for the PU molds. It is clear that the mold material and geometry (mold height in this study) significantly influence the values of the thermal parameters measured with the test methods described by the ASTM standard F-451.

Finite element parametric studies on the effects of mold material and height support the experimental observations. By best fitting the bone cement thermal test results in the 20 mm thick patty (which is not different from 40 mm, but require less materials) PU molds, the parameters of the bone cement kinetic models were obtained. Comparisons between the experimental data and the model predictions are shown in Figs. 3–6. Comparing the FE predictions with the experiments, the results indicate that the kinetic model well represents the polymerization behavior of the bone cement. In Figs. 5 and 6, the differences between measured and predicted setting time and setting temperature are very small: setting temperature is within less than 4 °C and setting time is within less than 40 s. In Figs. 3 and 4, for very high molds, the predicted setting temperature and setting

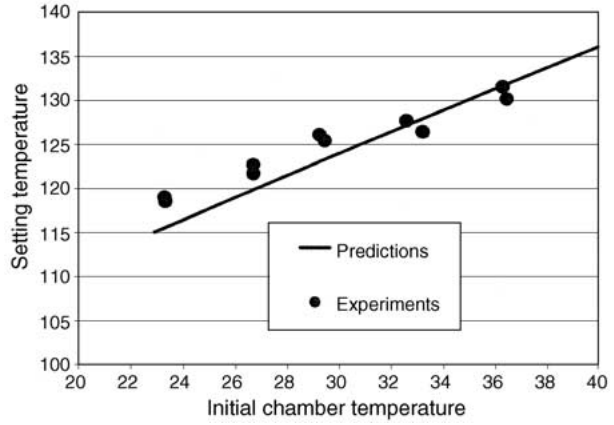

Figure 5 Cement setting temperature vs. chamber temperature: FEM predictions and experiments (20 mm thick PU mold).

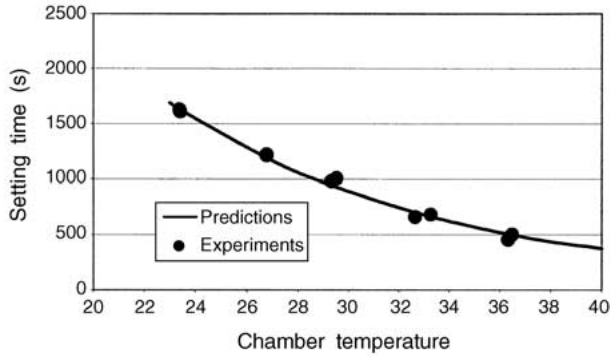

Figure 6 Cement setting time vs. chamber temperature: FEM predictions and experiments (20 mm thick PU mold).

time converge for the two different mold materials as observed experimentally. This is due to the nearly adiabatic conditions in the cement with very thick patties. The thinner the cement patties, the larger the difference between the predicted peak temperature and actual peak temperature with different mold materials. As shown in Fig. 3, in thin patties, the setting temperature predicted is very sensitive to the height of the molds. For the thick patties, the curves trend to a horizontal line, which indicates that the predicted peak temperature was nearly unchanged due to the good heat isolation. Such characteristics were also found in the curves predicting setting time, as shown in Fig. 4. As seen in both of these figures, the setting temperature and time are less sensitive to the height of the mold using PU foam as compared to PTFE materials. This is due to the poor heat conductivity of the PU foam. FE parametric studies on the effects of the mold material and geometry are consistent with the experimental observations.

In cemented orthopedics surgery, cement generates reaction heat due to polymerization. The amount of heat is related to the quantity of bone cement. It is well known that the heat will be lost to the surroundings by conduction and the conduction procedure is correlated with the system components' heat capacities and conductivities. Based on the kinetic model, increasing temperature will increase the reaction rate and the rate of heat evolution. The polymerization and heat conduction procedures are totally coupled. Similar situations can be found in industrial batch polymerizations and other exothermic chemical reactions. The methods outlined in this paper are preferred for more accurate measurement of curing parameters because of its better controlling of the effects of mold geometry and material on the thermal tests. It is expected that the method can be extended to thermal characterizations of other polymer materials.

4. Conclusion

In this study, experimental and numerical FE methods were used to characterize bone cement curing setting temperature and setting time. It was found that the mold materials and geometry significantly influence the values of these parameters measured with the ASTM standard method due to the heat transfer from the cement to the surrounding mold. Ignoring such heat conduction effects may underestimate the exothermic temperature of bone cement, which is a critical parameter associated with potential for thermal necrosis of bone. Thermal tests using higher mold or poor conductivity material molds can limit such effects and can provide more consistent experimental results. Significant results of the experimental work presented here include smaller measured variations in setting time and setting temperature for the modified mold. Using poor thermal conductivity materials for the test molds, while with the same mold geometry, is better for the characterization of bone cement polymerization thermal behavior. Improved consistency and reduced sensitivity to patty thickness (related to mold height) are distinct advantages for the modified cure test discussed. The modified cure test should reduce experimental error and thus provide a more reliable thermal characterization procedure.

It is assumed that the ASTM Standard F-451 was developed to mimic hip arthroplasty, where cement mantles are about 6 mm thick. As applications for injectable curing polymers expand, for example in vertebroplasty and kyphoplasty, thicker cement can be expected. Modeling of cement requires more careful characterization and thus the methods outlined here, i.e. using a 20 mm thick patty in a PU mold, are preferred for more accurate measurement of curing parameters.

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