

# Models for coupled kinetics and heat transfer in processing polymeric materials with applications to biochemical engineering

**Roderick V N Melnik**

University of Southern Denmark, MCI, Grundtvigs Alle 150, Sonderborg, DK-6400, Denmark

E-mail: [rmelnik@mci.sdu.dk](mailto:rmelnik@mci.sdu.dk)

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## Abstract

Macroscopic properties of thermosetting polymers are strongly affected by thermal degradation. However, modelling the dynamics of thermal degradation is difficult due to an intrinsic coupling between reaction kinetics and heat transfer in polymeric materials. In this paper we consider mathematical models for degradation focusing on thermal degradation and shrinkage phenomena. We discuss in detail a mathematical model that allows modelling thermal degradation as a coupled process and develop an efficient procedure for numerical studies of this process. The developed procedure is then applied to modelling degradation of acrylic resins widely used in chemical biomedical engineering. Results of numerical experiments are presented.

## 1. Introduction

The development of new materials is often impeded by the lack of sufficiently accurate models for process simulation and modelling [1]. To a large extent, this is explained by serious difficulties in modelling the dynamics of such materials due to an intrinsic coupling of several physical and chemical processes involved. One of the most important examples of this coupling is provided by a large class of materials which can be unified under the generic name ‘polymeric materials’ ranging from thermoplastics, thermosets, elastomers (rubbers, gels), polymeric composites (such as reinforced or filled polymers) to polymer colloids, polymer coatings and films, polymeric biomaterials, and to their variants such as copolymers and polymer blends. In particular, when modelling the *dynamics of degradation of these materials*, reaction kinetic and heat transfer should be considered as a *coupled process*. The importance of such a consideration is necessitated by a wide range of applications of the existing and a rapid development of new polymeric materials in general and polymeric networks in particular [2]. Many such new polymeric materials find a wide range of applications in chemical, biochemical, and biomedical engineering, e.g. in the form of polymeric composites containing thermosets

as their matrix components such as matrix resins based on epoxies, polyimides, etc. It is often emphasized that the analytical experimentations required for these materials are expensive and time consuming [3]. What is even more important is that such experimentations give us only snapshots from which it is difficult to deduce a dynamic behaviour of these materials. This leads to a situation where mathematical modelling tools becomes fundamentally important in this field.

In many important applications polymeric thermosetting materials become preferential to thermoplastic composites despite the fact that the fabrication of the latter is much faster. Recall that thermoplastic composites are usually made of long molecular chains by repeating monomer units, and they can be reheated and reshaped (and then cooled and rehardened) many times *without* changing the basic chemical structure [4]. This is not the case with thermosets, complex chemical structures that polymerize only when heated or cured with chemical agents. Unlike thermoplastics, thermosets change their chemical structure during processing. Moreover, such a change is typically irreversible, i.e. once polymerize they retain their shape forever. Due to this fact, the modelling of *dynamic behaviour of such materials accounting for the coupling* between chemical and thermal conditions of the processing becomes extremely important. In this paper we provide a general methodology for this modelling and give examples of computing thermochemical characteristics of acrylic resins, materials used in a wide range of chemical, biomedical and other engineering applications.

The paper is organized as follows. In section 2 we provide fundamentals of coupling effects induced by reaction kinetics and heat transfer in the context of those engineering applications where a coupled description becomes necessary. Experiment-based parametrization techniques for mathematical models in thermoset polymer processing are also discussed in this section. Section 3 focuses on the development of the general mathematical models of thermal degradation allowing to couple reaction kinetics and heat transfer. In section 4 we consider specific examples from bioengineering applications where coupling effects are key factors allowing to predict the onset of thermal degradation, and present results of computational experiments. Conclusions and future directions are discussed in section 5, while details of an efficient numerical procedure developed here are given in the appendix.

## **2. Mathematical modelling of thermoset polymer processing and experiment-based parametrizations**

Although typical thermosets are timely to process, they are much more stable and less likely to creep or soften at high temperature compared to such materials as thermoplastic composites. These properties are pivotal in such areas as communication industry, aerospace, electronics, biomedical engineering, and transportation, in particular in the encapsulation of computer chips, the development of polymer optical glass fibres for communication industry, mechanically strong glass fiber-reinforced thermoset composites for transportations, and new materials for orthodontistry to name just a few [5–10].

In many of these applications thermosets should be toughened. In the general case since the matrix resins in the thermoset composites can be viewed as ‘random mixtures of molecules cross-linked to one another’, the added toughness in un-reinforced resin and the toughness of the composite are subject to a complex nonlinear dependency (in some cases this nonlinearity is a consequence of the nonlinear polymer formation by cross-linking pre-existing chains of linear polymers as in thermoset epoxy polymers, or a consequence of the polymerization of the material before curing it). A typical toughened mixture consists of an epoxy solution, high molecular weight (MW) thermoplastic polymer precursors, and compatibilizers to help dissolve these two quantities in the solution. The curing of the epoxy requires heating of the

mixture in order to drive the solvent and compatibilizers off which leads to the elimination of the precursors from the solution and the formation of a cross-linked network. Within the network—a very small version of a reinforced composite—each resin system contributes its own properties to the final material. Heat transfer plays a fundamental role in the description of dynamic behaviour of these materials, and macroscopic properties of thermosetting polymers are strongly affected by thermal degradation. All the applications mentioned above require a coupling of the dynamics of heat transfer to chemical kinetics and such a coupling becomes a key factor in a better understanding of physics and chemistry of polymeric materials, in particular their degradation and stabilization.

Degradation of polymeric materials is an extremely complex process. Typically, this process involves primarily bond scissions in the macromolecule's backbone. Hence, it could be viewed as an opposite process to intermolecular cross-linking (where the new chemical bonds between individual macromolecules are created) that leads to some changes in physical properties, caused by a range of factors. Indeed, this 'range of factors' is one of the major difficulties in modelling this process because degradation can be initiated by several closely interconnected modes such as chemical, mechanical, biological, light-induced, electromagnetic, etc [11]. At the same time, studies of degradation become an intrinsic part of modelling polymeric materials processing where one has to (a) achieve some optimal conditions in the processing of polymers, (b) be able to predict the onset of their degradation, and (c) to propose an effective stabilization and control procedure at the processing stage. As a result, depending on temperature and other processing conditions one has to deal with different polymer morphologies, and polymer blends (mixtures of different kind of polymers with no covalent bonds between them) to get a stable polymer with the prescribed physical properties [12, 13]. Synergetic and/or antagonistic interactions between different quantities in the blends during degradation and between the products of degradation result in competing effects. These effects can lead either to an acceleration of the degradation rate (with respect to the degradation of pure components) or to a stabilising effect. A key factor that helps us to understand which one of the above two situations is more likely to happen is the temperature field. Therefore, it is important to model reaction kinetics in polymer processing as a *coupled thermochemical process*.

To emphasize further this point, recall that all organic macromolecules as well as low MW organic molecules are stable only below a certain limiting temperature, which is much lower compared to many inorganic materials. In principle, a high thermal sensitivity of organic substances can be explained at the molecular level because molecules are composed of atoms linked together by covalent bonds and the strength of these bonds is limited. Therefore, scissions of chemical bonds under the influence of heat are the result of overcoming bond dissociation energies. This fact has lead some researchers to applications of molecular modelling methodologies (see, for example, [2, 14] and references therein), and to the idea of tracing time- and rate-dependent thermochemical (and viscomechanical) properties of polymers back to their origin at a molecular level which has been refined in the methodology known as the group interaction modelling [15]. For the modelling at the macroscopic level our starting point lies with the fact that the behaviour and properties of polymeric materials are determined largely by processes of heat and mass transfer which, in their turn, depend strongly on the degradation reactions.

A number of experimental techniques have been developed to help predicting the onset of thermal degradation of polymers. Mathematical models we discuss here are complimentary to such techniques used as the basis for model parametrizations. Amongst such experimental techniques the three most popular techniques are: (a) the thermal volatilization analysis (TVA), consisting of trapping gaseous products followed by their characterization by such methods as

UV or mass spectroscopy, (b) the gel permeation chromatography where a change in molecular weight distribution (MWD) is detected upon main-chain rupture and/or cross-linking, and (c) the thermogravimetric (TG) analysis which is based on measuring the temperature dependence of the loss of sample weight due to the formation of volatile products. In the later case, the loss of weight at constant temperature is frequently measured as a function of time by recording vapour pressure changes in a closed system, and then the onset of degradation is characterized by the temperature at which it is possible to detect pressure changes [16]. Note that in reality the loss of weight is temperature dependent, and functional dependencies are used to incorporate this loss in mathematical models. Having TG and MW data, we can model the thermo-oxidative process to determine the kinetic parameters and the chain scission processes to predict the lifetime of the polymer. All such parameters in this paper were taken from the existing literature reporting such experiments (see, for example, [17] and references therein). It should be noted that although we use a single degradation function, our computer code has been developed for the case where the degradation kinetics could be modelled with any arbitrary number of degradation functions (examples of such functions can be found in [18]).

It should also be noted that reliable data on the *dynamic properties* of composite materials are sparse because of experimental difficulties associated with their determination, and experimental techniques to characterize the dynamic behaviour of composite materials is a subject of intense investigation [19]. Under these circumstances the development of *constructive procedures* for fully coupled mathematical models aimed at determining dynamic chemical (and, in some cases, viscomechanical) properties of polymeric materials become an extremely important task. However, dynamic models based on molecular simulations are often unpractical from a computational point of view for routine engineering runs, while usual analytical methods might fail in detecting chemical changes in polymer systems induced by their degradation (which often happens, for example, in those cases where the concentration of ‘weak links’ is low). Therefore, the development of macroscopic mathematical models and numerical methods for their solution that incorporate a coupled effect of chemical kinetics and heat transfer and allow prediction of such changes becomes a major avenue of research in this field [20].

Mathematical modelling can supplement efficiently experimental techniques in determining the onset of thermal degradation. Depending on a specific situation, degradation can be considered as having random or preferential character of main-chain scissions, and can be modelled numerically with stochastic or deterministic models. One of the simplest models is based on probabilistic arguments and the Schultz–Zimm form of the MWD taken as an initial approximation [11]. This and other similar models are based on the comparison of characteristics of the degradation process just at two different moments of time. As a result, such models cannot describe the realistic dynamics of the process, and therefore have a limited applicability.

Mathematical models capable of describing this dynamics should be derived on the differential equation basis. A simple dynamic rule could be derived as a generalization of simple probabilistic model mentioned above if we assume that *all* the products of degradation are included in the degree of polymerization calculation and that the rate of scission at time  $t$  is proportional to the number of unbroken bonds remaining. This generalization, known as the Kuhn–Freudenberg–Ekenstam model [21], can be represented in the following form

$$\frac{dU(t)}{dt} = kt, \quad (2.1)$$

where  $U(t)$  is the number of unbroken bonds at time  $t$  (i.e. the difference between the initial number of monomers,  $N(0)$ , and the number of monomers remaining at time  $t$ ,  $N(t)$ ), determined in turn as the ratio between  $N(0)$  and the degree of polymerization at time  $t$ ,  $D(t)$ .

It can be shown that in this case the random process describing degradation obeys simple dynamic rules of the standard first order kinetics of the following type  $1/D(t) - 1/D(0) = kt$ , noting herewith that most of such probabilistic mathematical models (including this one) for modelling polymer degradation are based on the assumption that scissions occur randomly within the polymer and there is an equal chance of breaking any bond [21]. The modelling of cross-linked, nonlinear polymers requires the development of more sophisticated models, accounting also for non-random (or systematic, or preferential) scission processes which tend to introduce 'curvature' leading to the situations where the first order kinetic models become no longer appropriate. Moreover, some degradation processes might require dealing with chain (self-propagating) reactions (in single-step processes, such as sylvolysis, the reaction rate is directly proportional to the rate of inflation, but for many processes such as autoxidation and depolarization the number of propagating steps could be very high). In all such cases probabilistic mathematical models discussed above should be improved.

Such improvements are intrinsically connected with accounting for coupling effects in the processing of polymeric materials. In addition to the coupling between reaction kinetics and heat transfer, mathematical models can provide further insight into the properties of polymeric materials by modelling thermochemical properties of thermosets effectively coupled to the modelling of such mechanical properties as stresses, which could ultimately lead to accurate prediction of shrinkage during thermoset curing. During curing, the structure of a polymeric system undergoes dramatic changes where the small-molecule system is transformed into a network. If this process proceeds at high conversions, the reaction mixture is completely insoluble and spectroscopic techniques (e.g. NMR) are ineffective. On the other hand, if the reaction rate is very slow, the rheological properties are relatively insensitive to changes in chemical structure. Therefore, the development of methodologies for assessing material performance over the entire range of cure is an important task in theory and applications of polymeric materials. Such a development is often originated from models for the cure-dependent molecular diffusion. Such models are often based on the dynamic dielectric analysis [22]. As the reaction in the curing system proceeds, the viscosity of the system increases rapidly due to chain growth and cross-linking, and as a result, the rate of reaction becomes increasingly dependent not only on the reactivities, but also on the diffusivities in the system as the molecular species collide and react (at high conversions, the rate of reaction is determined primarily by the mass transfer of the reactants). From a mathematical point of view this process can be described effectively by reaction-diffusion models. Note that during the curing process the chemical, mechanical, and electrical properties of the polymer attain their final values, and a substantial increase in the glass transition temperature can usually be observed as the resin approaches full cure. Therefore, in order to predict and control the properties of the final product and to characterize the processability of a thermosetting system in the general case, it is often important to formulate not only a quantitative kinetic model that is valid over the entire range of cure, but also a model predicting mechanical properties of the system (i.e. its shrinkage, residual stresses, etc). Such considerations would require a more detailed discussion on the dependency of the stress relaxation modulus on the MWD, the relaxation spectrum, and other characteristics (see, e.g. [23,24]). In the non-isothermal case one has to develop structure/property relationship in order to (a) track the extent of reaction with time, (b) relate the thermo-physical (viscoelastic) properties to that extent of reaction, and (c) calculate stresses in the component via a consistent constitutive equation. The starting point for constructing such a constitutive relation is a decomposition of the stress tensor,  $\sigma$ , into its deviatoric component  $\sigma_d$  and its bulk (diagonal) component  $\sigma_p$

$$\sigma = \sigma_d + \sigma_p \quad \text{with } \sigma_p = -\Delta PI, \quad (2.2)$$

where  $\Delta P = P - P_0$  is the thermodynamic pressure difference which under isothermal conditions can be determined according to known formulae that account for memory effects of the viscoelastic system [23]. Note also that (visco)mechanical properties of thermosets can often be modelled in the framework of linear viscoelasticity in a sense that constitutive equations are developed for relatively small strains (e.g. see [23] for a procedure allowing to compute the stress according to (2.2)). More complicated models of nonlinear viscoelasticity, which allow modelling shock propagation through epoxies, glassy cohesive failures and other important processes, are also available in the literature (see, for example, [25,26] and references therein). We emphasize that in all such cases the application of constitutive models like (2.2) is subject to the determination of the degree of reaction and temperature. Models that allow such a determination and numerical methods for their solution are discussed in the next sections.

### 3. Mathematical models of thermal degradation

In the processing of polymeric and composite materials heat transfer and chemical reaction are intrinsically related processes. Sometimes in the modelling of the processing of these materials as a first approximation we could consider these two processes as uncoupled. This, for example, could be the case in modelling such processes as injection moulding of thermoplastic polymers. The main focus in such problems is on heat transfer process (combined with the fluid flow modelling). Although uncoupled (in terms of heat transfer and chemical kinetics) models are still used in describing thermal cure of thermoset polymers [27], it should be emphasized that mathematical models for the processing of thermosetting polymers are intrinsically coupled and in that they are fundamentally different from mathematical models for the processing of thermoplastic polymers. It should also be noted that the quality of constitutive modelling with such formulae as (2.2) depends on a systematic coupled description of heat transfer and chemical kinetic processes. Due to applications of new technologies to increase heat stability of polymers (i.e. the increase of degree of crystallinity, intermolecular chemical cross-linking, etc), such coupled modelling methodologies become increasingly important as independent predictive tools [28], as well as complimentary tools to the existing experimental techniques discussed in section 2.

#### 3.1. Mathematical models of reaction kinetics

The determination of polymer degradation kinetics can be carried out effectively by mathematical tools based on the construction of kinetic equations (and using chemical information from, for example, TG experiments). In particular, the simplest mathematical model is based on the first order kinetic

$$\frac{d\alpha}{dt} = k_A(1 - \alpha), \quad (3.1)$$

where  $\alpha$  is the degree of reaction typically defined in terms of the ratio of the heat developed between the starting point and a given time  $t$  and the total heat developed [1], and  $k_A$  is the rate constant. Since in the general case the degradation of polymers is a multi-step process that involves sequential and competing processes, a system of the first order ODEs can be constructed easily if the number of components is larger than one [29]. In some cases it is sufficient to assume that the degradation process obeys the Arrhenius kinetics which allows us to connect the rate constant with the absolute temperature  $T$  and the activation energy  $\mathcal{E}_A$ :

$$k_A = A^* \exp\left(-\frac{\mathcal{E}_A}{RT}\right). \quad (3.2)$$

The ratio  $T_A = \mathcal{E}_A/R$  is often referred to as the activation temperature [30]. In the general case the value of  $A^*$  is dependent on the heating rate (i.e.  $A^* = A/H$  with  $H$  being the heating rate, and  $A$  the pre-exponential constant). Although the model (3.1), (3.2) can be used as a reasonable approximation for a number of epoxy resins (typically for those cases where the degree of cure is around 30%) there are many new resins where the conversion rates cannot be described by this model because of the higher (than one) empirical reaction orders.

If the empirical reaction order is not one, the process cannot be described by linear models like (3.1). For single-step degradation processes involving small samples a simple nonlinear model is often written in the form [30]

$$\frac{d\alpha}{dt} = k_A(1 - \alpha)^n, \quad (3.3)$$

where  $n$  is an additional degree of freedom in this empirical formula, and all other parameters have the same meanings as before. In this case, given the heating rate, one could say that the degradation can be characterized by three parameters,  $A$ ,  $T_A$ , and  $n$ . However, such models have well-known limitations on the magnitude of heating rate variations [30]. A straightforward generalization of models (3.1) and (3.3), often used for epoxies, can be written in the following form

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n, \quad (3.4)$$

where  $k_i$ ,  $i = 1, 2$ , are temperature-dependent reaction rate constants typically modelled by the Arrhenius law analogous to (3.2), and  $m$  is another experimental constant. Although this approximation is used widely in the literature, it should be noted that in describing epoxies, relaxation phenomena might play a significant role (i.e. when the epoxy vitrifies during cure, the reaction will slow dramatically and will deviate from the Arrhenius law). In such cases a possible approximation of the reaction rate coefficient could be given by the following expressions [23]

$$\tilde{k}_A = \frac{1}{1/k_A + C_3\tau_1}, \quad (3.5)$$

where  $\tau_1$  is the shortest relaxation time and  $C_3$  is a constant responsible for accounting the severity of the reaction quench due to vitrification.

Unfortunately, in many cases polymerization kinetics in thermoset composites during the cure process obeys a fairly complex rules which is difficult to model with (3.1)–(3.4) typically used in the literature. This should not come as a surprise if we recall that the cure kinetics of resins is determined by relating cross-linking (connected in a complex manner with conversion) and heat generation response due to time and temperature. The conclusion from this fact is that more degrees of freedom are required in our phenomenological models for kinetics to fit better experimental (TG) curves. In the general case not only one has to take into account the diffusion effect in these models and to couple the kinetic model with the energy balance equation, but also to account for the fact that depending on temperature conditions we can achieve usually only a partial resin cure (or conversion) due to quenching of the reaction [17, 31]. For these reasons we use a quite general model for the reaction kinetic with five degrees of freedom

$$\frac{d\alpha}{dt} = \tilde{K}\alpha^{\beta_1}(\alpha_{\max} - \alpha)^{\beta_2}(1 - \alpha)^{\beta_3}, \quad (3.6)$$

where  $\tilde{K}$  is a function of temperature determined as  $\tilde{K} = \tilde{K}_0 \exp(-\mathcal{E}_A/RT)$ ,  $\alpha$  is cumulative conversion (extent of cure) at a given time  $t$ ,  $\alpha_{\max}$  is the maximum conversion at a given isothermal cure temperature. Note that the partial conversion is accounted for by the term containing  $\beta_2$ , and the conversion rate is zero if  $\alpha = \alpha_{\max}$ . This term could also be written as

$(1 - \alpha/\alpha_T)^{\beta_2}$  with appropriate changes made to the pre-exponential coefficient  $\tilde{K}$ . In (3.6)  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  are exponents determined through the experiment.

Before proceeding to the heat transfer part of our models a few additional remarks should be made. Since their introduction as structural materials, composites have primarily been used for thin, laminated plates and shells (in particular, in the aerospace industry, where weight saving is critical). However, thick composites are also important in many industries [32]. There are inherent difficulties in manufacturing a thick-section polymer composites. A low thermal conductivity of thick thermosetting polymers presents a large barrier during heat-up and cool-down. In brief, these difficulties stem from the fact that as soon as the interior of the future product heats up, the exothermic curing reaction starts by releasing energy which is often trapped in the interior (due to poor thermal conductivity). Moreover, the entrapped heat raises the temperature of the interior even further, promoting faster curing and more rapid energy release. As a result, the process can quickly become unstable, in which case it is called a thermal spike phenomenon [32]. From a mathematical point of view such problems should be formulated as moving boundary problems. We note however that simple mathematical strategies have been already developed to determine the possible onset of spiking temperature during the curing of thermoset composite specimen [33]. Such strategies can be incorporated in the models we discuss. In all such cases it is useful to non-dimensionalize mathematical models [34]. For example, if we assume that the thickness of the cross-section of the product is  $L$ , the non-dimensional form of (3.1) can be written as

$$\frac{d\bar{\alpha}}{d\tau} = \bar{K}_0 \exp\left(-\frac{\bar{\mathcal{E}}_0}{1+\theta}\right) (1 - \bar{\alpha}), \quad (3.7)$$

where

$$\theta = \frac{T - T_0}{T_0}, \quad \tau = \frac{\alpha_e t}{L^2}, \quad \bar{\mathcal{E}}_0 = \frac{\mathcal{E}_0}{RT_0}, \quad \bar{K}_0 = \frac{K_0 L^2}{\alpha_e}, \quad (3.8)$$

$\alpha_e$  is the effective thermal diffusivity,  $\bar{K}_0$  is the Damköhler number coupling the chemical reaction with the diffusion phenomenon (it can be interpreted as the ratio of the conduction time scale ( $L^2/\alpha_e$ ) to the reaction time scale ( $1/K_0$ )).

Finally, we note that kinetic models can be formulated in terms of the mass fraction  $m$  (i.e. the ratio of the sample mass to the initial mass). Such formulations are often used for global ‘in-depth’ models of polymer degradation. If we apply kinetic equation similar to (3.3) (written in terms of  $m$ ) throughout the thickness of the specimen, a typical model (see, for example, [30] and references therein) can be reduced to a nonlinear integro-differential equation:

$$\frac{\partial m}{\partial \tau} + \bar{K}_0 \left\{ \int_x^1 m^{n-1} f(\theta) dx - (1-x) \int_0^1 m^{n-1} f(\theta) dx \right\} \frac{\partial m}{\partial x} = -\bar{K}_0 m^n f(\theta), \quad (3.9)$$

which is considered on the interval  $0 \leq x \leq 1$  and should be coupled to another (advection–diffusion type) integro-differential equation for the heat transfer. The resulting system is supplemented by appropriate initial and boundary conditions. In (3.9),  $f(\theta) = \exp(-\theta_A/(\theta + 1))$ ,  $\theta_A = T_A/T_0$  and other notation as before.

### 3.2. Heat transfer models

Manufacturing thermoset composites involve many processes. In most cases the cure is the most critical one, because it is an irreversible exothermic chemical reaction by which the composite lay-up is transformed from a soft, multi-layered mixture of fibers and resin, to a hard structural component. In order to model this process the chosen model for chemical kinetics should be coupled to a model for heat transfer. The starting point of such a coupling is



to establish an equation that connects the heat generation and the reaction (conversion) rates, i.e.  $dH/dt$  and  $d\alpha/dt$ , respectively. Recalling the definition of the reaction rate [1], it is quite natural to assume the linear dependency between these two quantities [17, 31], i.e. that

$$\frac{dH}{dt} = H_{\text{tot}}^r \frac{d\alpha}{dt}, \quad (3.10)$$

where  $H_{\text{tot}}^r$  is the total heat of reaction of the thermoset (resin) system,  $\alpha$  is the degree of cure. As we mentioned before, in many important situations the composites (reinforced plastics, thermosets) are used in the form of thin plates and shells, i.e. in the situation where one spatial direction (e.g. the axial direction  $z$ ) substantially exceeds the composite's thickness. As a result, it is sometimes appropriate to consider simplified one-dimensional heat transfer models for composite and polymer processing, for example,

$$\rho_p C_p \frac{\partial T}{\partial t} = \dot{q} + k_p \frac{\partial^2 T}{\partial z^2}, \quad (3.11)$$

where  $z$  is the distance along the axial direction,  $\rho_p$  is the density,  $C_p$  is the heat capacity coefficient and  $k_p$  is the coefficient of thermal conductivity of the polymeric material under consideration. It is assumed that the heat generation rate from exothermic reaction,  $\dot{q}$ , obeys the Fourier law which together with (3.10) leads to the following formula

$$\dot{q} = \rho_p \frac{dH}{dt} = \rho_p H_{\text{tot}}^r \frac{d\alpha}{dt}. \quad (3.12)$$

Depending on a specific situation the model for heat transfer should be supplemented by appropriate initial and boundary conditions (i.e. convection or prescribed temperature boundary conditions). A similar one-dimensional model has been recently applied for studies the processing of bone cement [17] (the material used in our computational examples). We write this model in the cylindrical coordinates as follows

$$\rho_{\text{cem}} C_{\text{cem}} \frac{\partial T}{\partial t} = k_{\text{cem}} \frac{1}{r} \frac{\partial T}{\partial r} + k_{\text{cem}} \frac{\partial^2 T}{\partial r^2} + \rho_{\text{cem}} \frac{dH}{dt}, \quad (3.13)$$

where all notation is as before with the index 'cem' indicating the type of polymeric material (bone cement).

More general situations in processing polymers and composites require applications of higher dimensional models for the heat transfer. Taken into account the representation of the heat generation rate via the reaction rate such models can be written in the following form [27]

$$\rho_{\text{cem}} C_{\text{cem}} \frac{\partial T}{\partial t} = \nabla(k_{\text{cem}} \nabla T) + \rho_{\text{cem}} H_{\text{tot}}^r \frac{d\alpha}{dt}. \quad (3.14)$$

Using arguments similar to those used for (3.7) and (3.8), this model can be non-dimensionalized and in the two-dimensional case instead of (3.14) one can consider the following model (i.e. [34])

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial}{\partial \bar{x}} \left( \bar{k} \frac{\partial \theta}{\partial \bar{x}} \right) + \frac{\partial}{\partial \bar{y}} \left( \bar{k} \frac{\partial \theta}{\partial \bar{y}} \right) + B_0 \left( \frac{d\alpha}{d\tau} \right), \quad (3.15)$$

where the non-dimensional variables given by

$$\bar{x} = \frac{x}{L}, \quad \bar{y} = \frac{y}{L}, \quad \bar{k} = \frac{k}{k_e}, \quad (3.16)$$

$k_e$  is the effective thermal conductivity and  $B_0$  is an adiabatic reaction temperature, which represents the temperature rise potential due to the heat of the reaction. Other notations remain the same as those in (3.7) and (3.8). Now we are in a position to analyse computationally the coupled reaction and heat transfer in processing polymeric materials.

#### 4. Coupled models for reaction kinetics and heat transfer in bioengineering applications

The models discussed in the previous sections have been applied to modelling the dynamics of several different polymeric materials that undergo processing. Here we report some results on mathematical and computational aspects of modelling the processing of acrylic bone cement, one of the most widely used materials in a number of medical practices, in particular orthopaedics. This material allows a fairly quick fixation of the implant, it is ‘surgically forgiving’ and can easily be removed prior to revision arthroplasty [35]. One of the key research directions in this field of chemical bioengineering is the modelling of the processing of acrylic cement in the context of prosthesis–cement–bone structures which is closely connected with the developing cement failure criteria [35]. We focus here on those bioengineering applications where bone cement is used to fix a prosthesis in a bone, that is where a typical geometry can be given by figure 1. A hollow axisymmetric cylinder depicted in figure 1 mimics a bone cement cover of a bone.

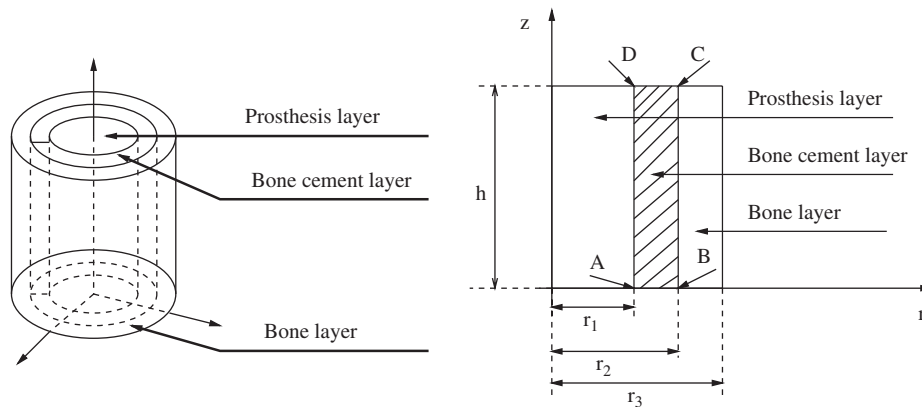
The heat transfer can be modelled by the two-dimensional model derived from (3.14) and (3.10) in the case of cylindrical coordinates

$$r\rho_{\text{cem}}C_{\text{cem}}\frac{\partial T}{\partial t} = \frac{\partial}{\partial r}\left(rk_{\text{cem}}\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial z}\left(rk_{\text{cem}}\frac{\partial T}{\partial z}\right) + r\rho_{\text{cem}}H_{\text{tot}}^r(x, z, t, T)\frac{d\alpha}{dt}. \quad (4.1)$$

Equation (4.1) is coupled to the general equation (3.6) for the reaction rate. The basic parameters for our reaction kinetics model, obtained from calorimetric measurements (see [17] for details), are given in table 1. The model (3.6) has been parameterized as follows

$$\begin{aligned} \tilde{K}_0 &= 4.76 \times 10^9, & T_A &= 8207, & \alpha_{\text{max}} &= 0.018T - 5.034, \\ \beta_1 &= 0.7, & \beta_2 &= 0.9, & \beta_3 &= 1. \end{aligned} \quad (4.2)$$

The coupling between model (4.1) and the model for reaction kinetics (3.6) is also pronounced via the definition of coefficients of model (4.1), in particular the specific heat



**Figure 1.** Basic geometry of the computational region and notation.

**Table 1.** Parametrization of the reaction kinetics.

Parameter	Units	Value	Parameter	Units	Value
$\rho_{\text{cem}}$	$\text{kg m}^{-3}$	1100	$k_{\text{cem}}$	$\text{W m}^{-1} \text{K}^{-1}$	0.17
$K_0$	$\text{s}^{-1}$	$4.76 \times 10^9$	$\mathcal{E}_A$	$\text{J mol}^{-1}$	$71.41 \times 10^3$
$R$	$\text{J mol}^{-1} \text{K}^{-1}$	8.314 472	$H_{\text{tot}}^r$	$\text{J g}^{-1}$	152

coefficient. Using typical experimental curves, it is easy to conclude that the (effective volumetric) specific heat for composites (consisting from fibers and matrices) can be represented in the form [34]

$$C_p \equiv C_p(\alpha, T) = C_p^1 \alpha + C_p^2 (1 - \alpha), \quad (4.3)$$

where in the most general case both coefficients  $C_p^1$  and  $C_p^2$  are temperature-dependent functions. In this paper the specific form for  $C_p$  was obtained from the interpretation of (4.3) as the sum of two terms accounting for contributions before and after polymerization (we used the data from figure 10 in [17] and approximated both coefficients  $C_p^i$ ,  $i = 1, 2$  by linear functions of temperature, in which case (4.3) should be taken in  $\text{J kg}^{-1} \text{K}$  units)

$$C_p^1 = 629.10 + 3.30T, \quad C_p^2 = -6650.00 + 22.47T. \quad (4.4)$$

The problem is supplemented by initial and boundary conditions as explained below. Since our main interest lies with the intermediate layer (i.e. the cement layer) of the structure depicted in figure 1, we use the following arguments to simplify the problem.

Firstly, it is well known that temperature at the prosthesis–cement interface remains practically unchanged. Therefore, it is appropriate to impose Dirichlet boundary conditions ( $T = T_{\text{pros}}$ ) at the boundary [AD] (see figure 1). Note that since the thermal conductivity of prosthesis is more than 60 times larger than the thermal conductivity of cement (see table 2), the prosthesis acts just as a heat sink for heat dynamics in the cement layer and the imposed Dirichlet condition is quite natural (this is not the case for the interface between bone and cement because the thermal conductivity of the bone is comparable with the thermal conductivity of cement and an approximation to the thermal exchange condition is required). Secondly, the Neumann boundary conditions ( $\partial T / \partial z = 0$ ) are imposed at boundaries [AB] and [CD] (ALTPACK allows to impose other boundary conditions if required [36]). Finally, boundary conditions at the cement–bone interface has been approximated using the heat flux continuity assumption

$$k_{\text{cem}} \frac{\partial T}{\partial r} = k_{\text{bone}} \frac{\partial T}{\partial r} \quad \text{for } r = r_2. \quad (4.5)$$

If temperature of the bone at  $r = r_3$  is  $T_{\text{bone}}$  and the effective thickness,  $\Delta h = r_3 - r_2$ , is relatively small, in most practical situations it is appropriate to approximate the derivative in the right-hand side of (4.5) by the left difference derivative  $(T_{\text{bone}} - T_{\text{cem}}) / \Delta h$  which leads to the following approximation of the boundary condition for temperature at [BC]

$$-\frac{\partial T}{\partial r} = (T - T_{\text{bone}}) \frac{k_{\text{bone}}}{k_{\text{cem}} \Delta h}. \quad (4.6)$$

The initial temperatures of prosthesis and bone are assumed to be at  $T_{\text{pros}}$  and  $T_{\text{bone}}$ , respectively. Assuming linearity of temperature in  $r$  inside of the cement layer at the initial moment of time, it is easy to derive the following approximation for the initial condition ( $t = 0$ )

$$T = ar + c \quad a = \frac{T_{\text{bone}} - T_{\text{pros}}}{\Delta r}, \quad c = T_{\text{bone}} - \frac{(T_{\text{bone}} - T_{\text{pros}})r_2}{\Delta r}, \quad (4.7)$$

**Table 2.** Data for the initial and boundary conditions and the geometry of the problem.

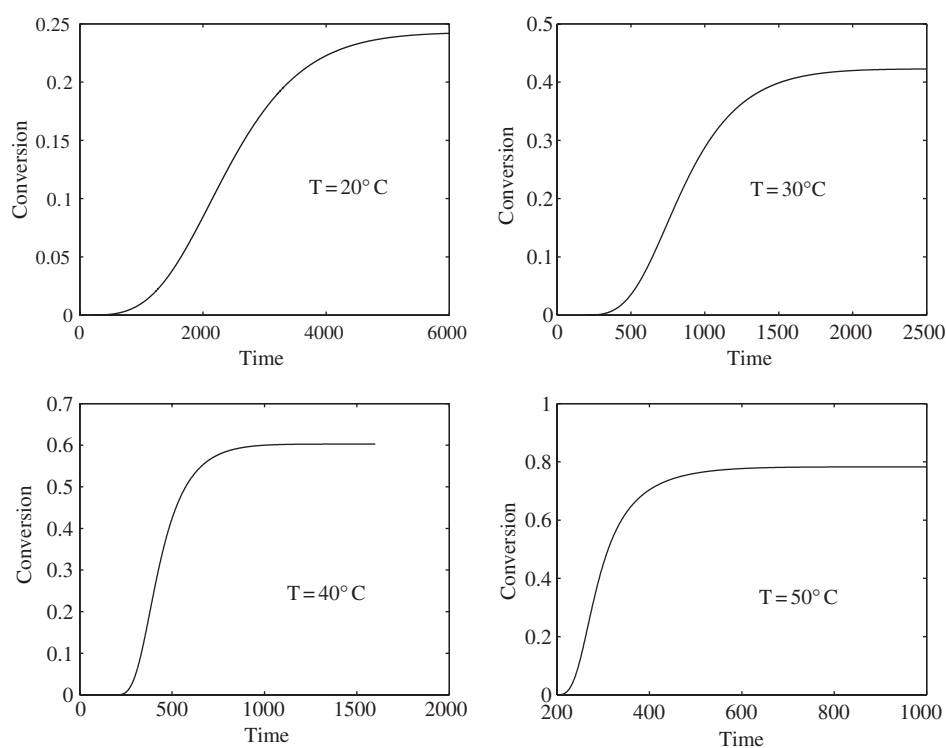
Parameter	Units	Value	Parameter	Units	Value
$r_1$	m	$8.0 \times 10^{-3}$	$T_{\text{bone}}$	K	310.0
$r_2$	m	$13.0 \times 10^{-3}$	$T_{\text{pros}}$	K	293.0
$r_3$	m	$18.0 \times 10^{-3}$	$h$	m	$10.0 \times 10^{-3}$
$k_{\text{bone}}$	$\text{W m}^{-1} \text{K}^{-1}$	0.43	$k_{\text{pros}}$	$\text{W m}^{-1} \text{K}^{-1}$	10.3

where  $\Delta r = r_2 - r_1$ . Approximations of boundary and initial conditions that differ from those described above can also be easily implemented into the code (see [36] for details).

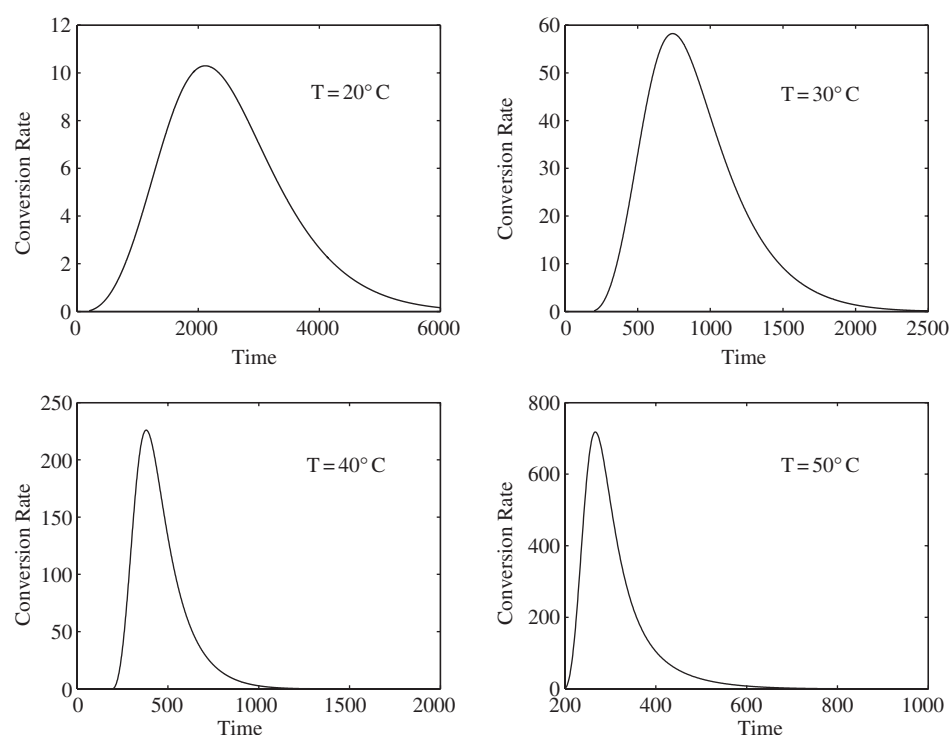
The coupled system of equations (4.1) and (3.6) with appropriate initial and boundary conditions is solved in this paper in an efficient iterative manner (see appendix).

The values of parameters used in our computational experiments for the initial and boundary conditions and the geometry of the problem are summarized in table 2.

The first group of experiments have been designed to monitor the reaction dynamics under elevated temperature. The experiments were conducted with kinetic model (3.6) where the reaction kinetics can be formally uncoupled from the heat transfer. At the initial moment of time, the conversion can be assumed practically negligible (taken at  $10^{-5}$ ). The dynamics of conversion can be described by solving approximately the differential equation (3.6). All values chosen for the experiments reported here were taken from tables 1 and 2. In figure 2 we plotted kinetic curves (i.e. conversion vs cure time) obtained for gradually increasing temperatures. As expected, the maximum conversion rate in all reported cases is less than 1 which indicates that the reaction is completed only partly and a part of non-polymerized material is still present in the structure. In this case, the model for  $\alpha_{\max}$  plays a key role in determining the onset of stabilization for the conversion processes. Another important characteristic of the kinetic process is the conversion rate. We present results on computing this characteristic in figure 3. The figure demonstrates clearly that under increasing temperature the conversion rate peak is shifted to the left being in a good agreement with results previously obtained in the literature with differential scanning calorimetry techniques (e.g. [17]).



**Figure 2.** Conversion evolution for different temperatures (time units are given in seconds).



**Figure 3.** Evolution of the conversion rate for different temperatures (time units are given in seconds).

Since unreacted material can be polymerized by heating, it is important to know the spatial distribution of temperature when the coupling between the heat transfer and reaction kinetics is fully accounted for. This was investigated in the second group of experiments. The results of computations of the temperature field with the coupled model are plotted for different moments of time in figure 4. Here we start from linear (in  $r$ ) profile of temperature and almost zero degree of conversion. Due to a higher temperature at the cement–bone interface, conversion and temperature start increasing driving the curing process to inside of the cement sample. Due to a lower temperature at the prosthesis–cement interface curing slows down at that end. Since requirements of minimising the peak of temperature and maximising the degree of curing compete with each other, after a while temperature becomes almost linear again, whereas conversion exhibits a typical spatial pattern presented in figure 5. This indicates that the degree of conversion can be controlled by thermal field and by the boundaries. Although these plots are very helpful in determining locations of peak temperature in the structure, they do not provide information on how such peaks propagate in time. This characteristic of the process, presented in figure 6, is very important in preventing thermal spiking phenomena in structures where the thickness of the bone cement layer is comparable with other dimensions.

## 5. Conclusions and future directions

In order to model and control accurately the properties of the final product in polymer and composite processing, it is necessary to formulate a quantitative kinetic model that is valid over the entire range of cure and then to couple that model to models for heat transfer. In this paper, we have reported results on mathematical and numerical modelling of the dynamic

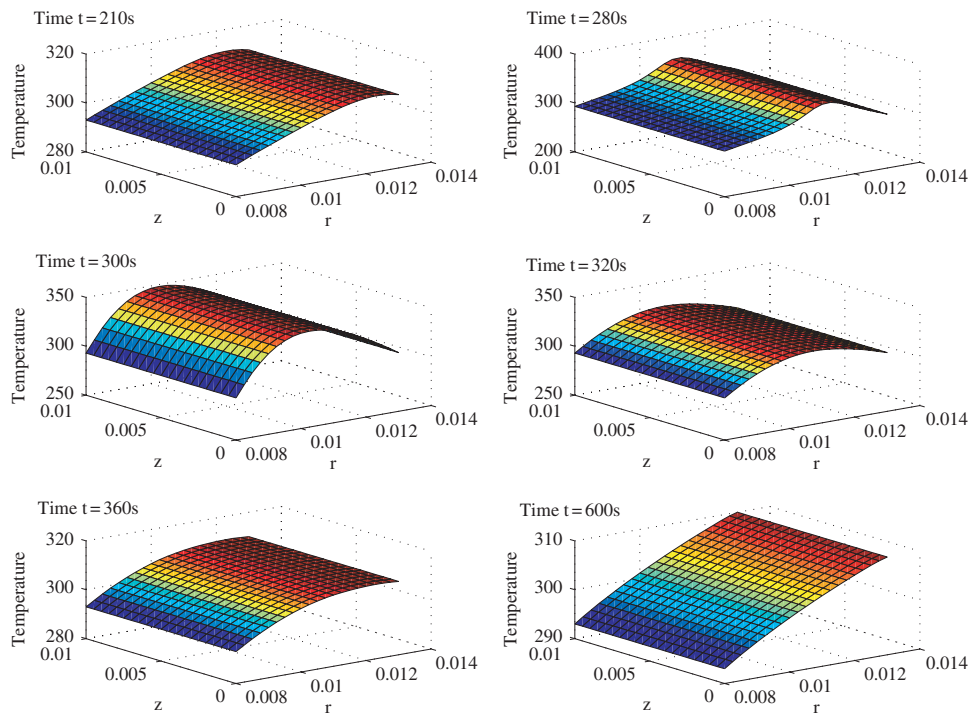


Figure 4. Spatial distribution of temperature evolving in time.

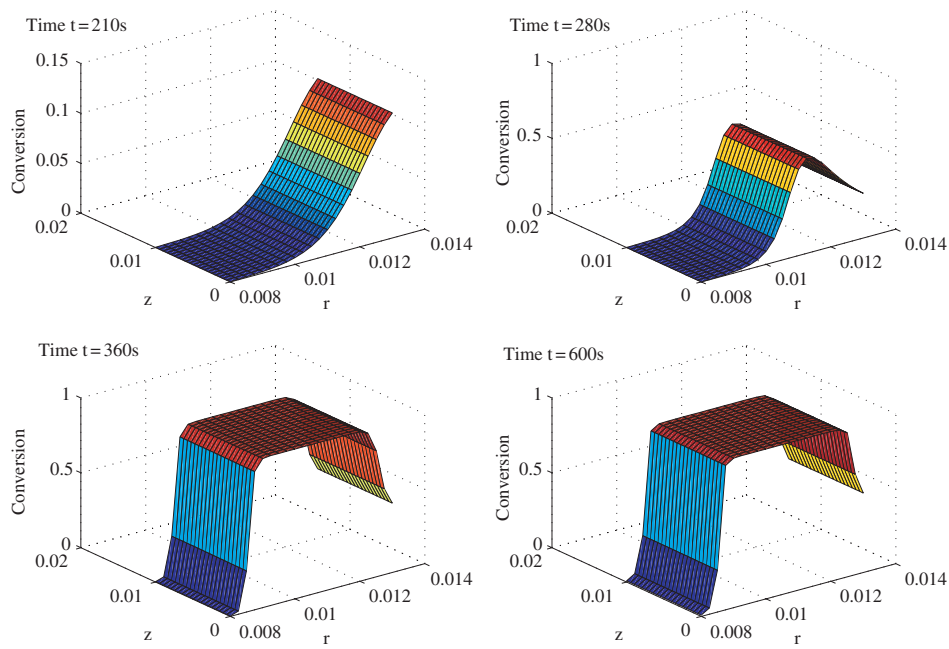
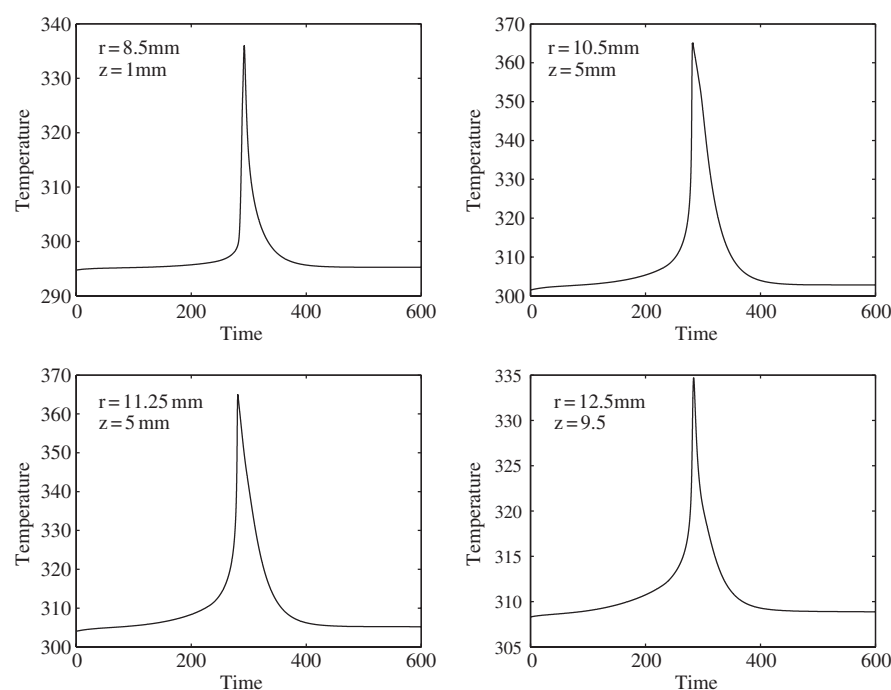


Figure 5. Spatial distribution of conversion evolving in time.



**Figure 6.** Temperature dynamics in the bone cement part of the structure (time units are given in seconds).

characteristics of such coupled processes. Numerical algorithms developed in this paper may prove to be useful in modelling polymer processing, including batch processes, autoclave curing, and a number of continuous processes such as pultrusion [34].

Our specific, but at the same time, generic examples were given for the acrylic cement which is rated highly (compared to many other polymeric materials) in many biomedical applications. However, this material has also some drawbacks (resulting in the possibility of aseptic loosening), which could be addressed by some combination of the technique described in this paper with topological models [2]. Such combined models may provide a better insight into a well-known problem connected with the contribution of the acrylic cement to thermal and/or chemical necrosis of the bone, and its predisposition to membrane formation at the cement–bone interface (which under certain conditions might shrink during polymerization). A closely related direction for the development of the presented work lies with the fact that the (thermo)mechanical behaviour of composite materials does not depend on the properties of each components (matrix and filler or fiber) only, but also on their interface. For the thermoset matrices, the structure of the interphases is dependent on the chemical reactions between the surface and the reactive mixture during the processing [37]. Efficient models for these processes as well as models for phase separations in thermoset–thermoplastic polymer blends, and phase transitions of polymer liquids and alloys are at early stages of their development [38, 39].

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## Appendix

First, taking temperature from the initial condition (4.7) we solve the kinetic reaction equation and determine, as a result,  $d\alpha/dt$  at time  $t_1 = t_0 + \tau$  for all spatial points (note that the kinetic reaction rate is a spatially-dependent function). The value of the conversion rate,  $d\alpha/dt$ , will serve as the input for the package ALTPACK which solves the equation (4.1) and hence determines the temperature at the new time layer.

We use ALTPACK for coupled dynamic calculations where the key subroutine `polymer.f` is an adaptation of the code described in details in [36]. The code implements the alternating-triangular algorithm for the solution of general nonlinear evolutionary equations with parabolic operator. The code utilizes the procedure of ordering for Chebyshev iterative parameters that allows us to minimize the influence of round-off errors and to eliminate large intermediate values dependent on the number of iterations in the computational procedure. In addition, the code can treat effectively problems with fast varying coefficients (which is important in the problems considered here), and tends to be more economical computationally compared to the classical implicit methods of alternating directions such as ADI.

The reaction kinetic equation is solved with a two-step block Runge–Kutta–Fehlberg (RKFC) procedure called `kinetics.f` that uses interpolation to produce output at ‘off-step points’ efficiently. This is a modified procedure developed originally by J R Cash and H A Watts (see Netlib Software Library). In the context of our problem, the starting point of computations with this model has to be chosen greater than zero. The result of computation of the conversion rate (stored in the array  $Y_p$ ) is fed into the right-hand side ( $F_p$ ) in `polymer.f` (note that  $F_p = \rho r Y_p$  and the results presented here were scaled by factor 3.5; the detailed description of ALTPACK is given in [36]). If required, an arbitrary number of equations can be solved with `kinetics.f` (see comments followed equation (3.1) in section 3.1).

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