POLYMERIZATION KINETICS OF ACRYLIC BONE CEMENTS BY DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

Bone cements are widely used for the fixation of metallic prostheses in orthopaedics and to form replacements for skull defects in neurosurgery. Acrylic bone cements are based on a mixture of methyl methacrylate (MMA) and a fine powder of polymethyl methacrylate (PMMA). The polymerization of the bone cement occurs in contact with the bone and the prosthesis which act as the boundaries of a bulk polymerization reactor. The kinetic behaviour of the bone cement plays a fundamental role for the final performance of the implant.

In this paper, the isothermal and non-isothermal polymerization behaviour of a commercial bone cement is described. A simple phenomenological model, accounting for the autoacceleration effect, for a diffusion controlled termination mechanism and for the reaction between inhibitor and initiator, is proposed. The reaction kinetics is analysed by DSC. DSC data are used for the determination of the rates of polymerization under isothermal and non-isothermal conditions. The experimental data are processed to calculate the parameters of the proposed phenomenological kinetic model. The analytical and numerical details related to the integration of the model are discussed.

Keywords: bone cement, DSC, kinetics

Introduction

The fixation of metallic prostheses in orthopaedics and the restoration of skull defects in neurosurgery are usually achieved by poly(methyl methacrylate)-based bone cements which polymerize 'in situ' [1]. In the case of a total hip replacement, the bone cement, inserted in a femoral axial cavity appropriately drilled by the surgeon, acts as a bonding agent between the prosthesis and the bone. Acrylic bone cements are based on a mixture of methyl methacrylate (MMA) and a large fraction of a polymeric fine powder of polymethyl methacrylate (PMMA) and/or polystyrene (PS). Barium sulphate is often added in small fractions in order to obtain a radiopaque material. The liquid MMA and the solid polymeric powder are mixed by the surgeon and inserted in the bone cavity where the polymerization reaction occurs. During its application, the bone and the prosthesis act as the boundaries of a bulk polymerization reac-
tor. As a consequence of the development of significant heat due to the exothermic nature of the polymerization reaction, a fast and highly non-isothermal bulk polymerization occurs. Furthermore, incomplete polymerization occurring in normal operative conditions may result in high levels of unreacted monomers in the cement. The residual MMA, slowly released from the cement, may be responsible for tissue damages. Tissue necrosis, caused by chemical or thermal causes effects, is a key factor for a good adhesion between the bone and the cement. For these reasons the properties and the performances of methyl methacrylate (MMA)-based bone cements are strongly dependent on their polymerization kinetics.

Furthermore, the peculiar characteristics of the polymerization environment require a short time for the completion of the reaction (typically 10–15 min at the body temperature) [1]. The initiation of the polymerization at low temperature is achieved by using a redox system such as amine-peroxide. The addition of a tertiary amine to peroxide initiators may increase the rate of production of radicals by several orders of magnitude at temperature lower then 50°C [2].

Bulk polymerization of MMA is greatly affected by diffusion at low and high values of the degree of reaction. In the first case, formation of high molecular weight molecules is responsible for a reduction in mobility of the chain end radicals resulting in a dramatic increase in the rate or reaction (‘autoacceleration effect’ or ‘gel effect’). In the second case, the transition from a high-viscosity rubbery polymer to a glassy polymer (vitrification), strongly affects the polymerization kinetics causing the reaction to stop. In fact, the glass transition temperature, continuously increasing during cure, approaches the isothermal cure temperature thereby strongly reducing the molecular mobility. Under these conditions, the reaction becomes diffusion controlled and the termination step of the polymerization is governed by the strong reduction in the molecular mobility caused by vitrification [3–5].

Although the bulk polymerization of MMA has been widely studied [3, 6–10], the polymerization kinetics of bone cements is characterised by unique features as a consequence of the diffusion effects induced by the high fraction of polymeric filler. The addition of a solid polymer to the reactive medium enhances the rate of reaction acting on the onset of the so-called ‘autoacceleration effect’ or ‘gel effect’ [2, 3, 8, 10]. The autoacceleration effect is related to the viscosity of the reactive medium and can be observed at higher degrees of reaction when a non-reactive solvent is added to the monomer [2]. On the other hand, the higher the amount of polymeric filler added to the monomer the lower the onset temperature of the autoacceleration effect [9]. These experimental results indicate that the added polymer and the polymer formed during polymerization act in an equivalent way on the onset of the autoacceleration effect. Therefore the autoacceleration effect is exploited in the bone cements in order to decrease the reaction time, by inducing an accelerated reaction kinetics compared with pure MMA.

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