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# Influence of P/L ratio and peroxide/amine concentrations on shrinkage-strain kinetics during setting of PMMA/MMA biomaterial formulations

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**Abstract**

This study investigated the effects on polymerisation shrinkage-strain for two unmodified powder and liquid formulations of polymethyl methacrylate (PMMA), methyl methacrylate (MMA) dough-type systems, by varying the powder/liquid (P/L) ratio. Furthermore, the shrinkage-strain effects for the 1.0:1.0 P/L ratio of adding additional amounts of amine and benzoyl peroxide (BPO) were studied. The rationale was the continuing importance of bone cements and the renewed interest in acrylic biomaterials, based on MMA and PMMA co-polymers, as used in new fibre-reinforced systems, where low P/L ratios may be important. Shrinkage-strain is directly related to extent of monomer conversion and has intrinsic importance related to interfacial disruption. Shrinkage-strain kinetics were determined using the "bonded disk" method. The first series of experiments studied two unmodified self-curing materials (MEA and PAL), where specimens with different P/L ratios by volume (3.0, 2.5, 2.0, 1.5 and 1.0 to 1.0) were mixed for 60 s. In these formulations, final shrinkage-strain values correlated positively with P/L ratios, rather than negatively, as would be expected from fully polymerised material. This highlights a problem of under-polymerisation through deviation from an optimum or recommended P/L ratio. When an additional 1.0% BPO was added in the powder, final shrinkage-strain values correlated negatively rather than positively, with P/L ratio for both products, except at ratio 1.0:1.0. Specimens mixed at 1.0:1.0 P/L ratio, with increasing amounts of BPO and amine resulted in higher final shrinkage-strain values, indicative of more complete polymerisation. Shrinkage-strain and optimum polymerisation are related, but clinically rather antagonist properties with respect to effective biomaterial utilisation and performance. In both design and surgical application of these polymethacrylate formulations, possible adverse effects of changing P/L ratio, producing either excessive shrinkage-strain or under-polymerisation, must be understood and where possible controlled.


*Keywords:* Polymerisation; Shrinkage; Bone cement; Polymethyl methacrylate; Degree of conversion; Initiator; Powder/Liquid ratio

## 1. Introduction

Self-curing polymethyl methacrylate (PMMA) cements have been used extensively as orthopaedic bone cements and in dentistry. Often termed acrylic cements, they are mainly used in the form of a two-component self-polymerising system, consisting of a powder and a liquid that are mixed in room temperature. The powdered part contains mainly PMMA, currently the principal material used in arthroplasties for anchoring cemented implants to the contiguous bones [1]. The mixed form is used for ease of handling and to minimise shrinkage-strain upon polymerisation through progressive substitution of pre-polymerised powder for quantities of liquid monomer. The formulations include a catalyst such as benzoyl peroxide (BPO), and often pigments and/or radiopacifiers such as barium sulphate ($BaSO_4$). The liquid part contains methyl methacrylate (MMA) monomer, a cross-linking agent (EGDMA), an amine such as *N*,*N*-dimethyl-*p*-toluidine (DMPT) used as an initiator and hydroquinone as an inhibitor. Acrylic or PMMA resins have been used in dental applications with three main activation types: heat-curing, self-curing and light-curing. In heat-cured acrylic

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resins, polymerisation is initiated by free radicals from the BPO which is activated by thermal decomposition of BPO [2]. In self-curing, the polymerisation reaction of methacrylate monomers is initiated by the activation reaction of BPO, with an amine accelerator at room temperature which gives free radicals for addition to monomer molecules [3]. In light-curing, a suitable photo-initiator such as camphoroquinone is irradiated with blue light to produce free radicals in the presence of amine and monomer.

Susceptibilities to various mechanically disruptive factors are especially important in compromising the structural integrity of orthopaedic bone cement [4]. Such problems as dynamic creep and fatigue response may be exacerbated by shrinkage-strain of the cement during polymerisation, which may from the outset induce local strains and/or stresses so reducing optimum interfacial load transfer between the bone and bone cement [5]. The polymerisation shrinkage-strain of the PMMA/MMA used for repairing fractured dentures, can sometimes cause distortion, leading to poorly fitting prostheses [6]. As noted below, the shrinkage-strain of MMA upon polymerisation is 21.1%. Such a high polymerisation shrinkage-strain can be reduced by admixing PMMA powder with MMA liquid, since only the MMA component shrinks during polymerisation. Gilbert et al. [7] have attributed porosity of bone cements, when setting under constraint, partly to the effect of polymerisation shrinkage-strain. Recently, powder/liquid (P/L) ratio-effects on some material properties of the PMMA/MMA systems have been reported [8]. In a study on autopolymerising PMMA, Rose et al. [9] showed that increasing amounts of BPO initiator in the powder and (DMPT) amine in the liquid increased the *rate* of polymerisation and the magnitude of the exothermic temperature. Lately, a renewed interest has arisen in acrylic biomaterials, based on MMA and PMMA copolymers, for applications in fibre-reinforced systems, where low P/L ratios may be important. Vallittu [6] used glass fibres as acrylic resin strengtheners and varied the ratio of PMMA–MMA in the mixture, finding that less PMMA powder results in higher shrinkage-strain and is thus a less suitable formulation. None of these valuable studies included a comprehensive evaluation of shrinkage-strain kinetics over a wide range of P/L ratio for the PMMA/MMA system.

The primary aim of this research was to determine the variation of polymerisation shrinkage-strain of two self-cure acrylic biomaterials incorporating PMMA and MMA with different P/L ratios. The effects of the addition of known amounts of BPO initiator and DMPT co-initiator on shrinkage-strain were examined as factors affecting polymerisation extent and also in view of initial trends in shrinkage-strain observed with P/L variation.

### *1.1. Theoretical relationship between conversion and shrinkage-strain*

In the polymer science literature it is widely accepted that the dominant cause of shrinkage-strain in monomethacrylates arises from conversion of C=C double bonds, where for each monomer segment of the chain the larger van der Waals inter-molecular spacing is replaced by the smaller intra-molecular covalent bond [10,11]. This results in density changes on proceeding from monomer to polymer [7]. Thus an exact semi-empirical relationship can be derived. Experimentally, the volume change per mole of methacrylate groups (C=C) in MMA is $\Delta V_{C=C} = 22.5\,\mathrm{cm}^3/\mathrm{mol}$ (or $10^{-6}\,\mathrm{m}^3/\mathrm{mol}$) [9,10] when MMA is polymerised. The molar volume of MMA is

$$\frac{M_m}{\rho_m} = \frac{100.12}{0.94} = 106.51\ \mathrm{cm}^3.$$

Hence, the volumetric shrinkage-strain of MMA is $\frac{22.5}{106.5} \times 100 = 21.12\%$, Here, $M_m$ is the molecular weight and $\rho_m$ is the density.

The values for density and molecular weight were obtained from the Polymer Handbook [12]. In the more general case of multi-methacrylates, where $f$ is the *functionality* of the monomer, the number of functional groups present in volume ($V$) is

$$\left[f \times \frac{V\rho_m}{M_m}\right].$$

The number of functional groups *reacted* in volume ($V$) is

$$\mathrm{DC} \times \left[f \times \frac{V\rho_m}{M_m}\right],$$

where DC is the fractional *degree of conversion*.

The percentage relative change in volume (volumetric shrinkage-strain) is

$$\frac{\Delta V}{V}(\%) = 22.5 \times \mathrm{DC} \times f \times \frac{V\rho_m}{M_m} \times 100. \quad (1)$$

For a mixture of monomers of any functionality

$$\frac{\Delta V}{V}(\%) = 22.5 \times \mathrm{DC}_{mix} \frac{\sum_i (f_i \chi_i)}{\sum_i (M_{mi} \chi_i)} \rho_{mix} 100, \quad (2)$$

where $f_i$ is the functionality of monomer ($i$), $\chi_i$ is mole fraction of monomer ($i$), $M_{mi}$ is molecular mass of monomer ($i$) and $\rho_{mix}$ is density of the monomer mixture.

For example, with two monomers, one monofunctional and one difunctional

$$\frac{\Delta V}{V}(\%) = 22.5 \times \mathrm{DC}_{mix} \left[\frac{2\chi_1 + \chi_2}{M_{m1}\chi_1 + M_{m2}\chi_2}\right] \times \rho_{mix} \times 100. \quad (3)$$

Eqs. (1)–(3) embody the expectation that the volumetric shrinkage-strain will be directly proportional to the