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Feature article

Fabrication of ceramic microneedles – The role of specific interactions between processing additives and the surface of oxide particles in Epoxy Gel Casting

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ABSTRACT

Epoxy Gel Casting (EGC) was recently coined to designate a setting mechanism based on the *in situ* polymerization of epoxy resins dissolved in the aqueous dispersion media of ceramic powder suspensions upon adding suitable amine-based crosslinking agents. The specific interactions between the surface of the powder particles and the processing additives are likely to determine different partitions of the crosslinking species, dissolved in the bulk solution, or adsorbed at the surface of the particles, and affect the EGC process. The present work aims at evaluating the influence of surface chemistry on the extent of the specific interactions at the solid/liquid interface and how it affects the polymerization kinetics and the properties of ceramic green bodies consolidated by EGC. Three different ceramic oxides (alumina, zirconia and fused silica) having similar particle size distributions were used. Stable colloidal suspensions with 45 vol.% solids were prepared by dispersing the powders in aqueous solutions containing a fixed amount of a common dispersant and various dissolved amounts of an epoxy resin. Zeta potential, rheological measurements and calorimetry were used to assess the specific interactions and their effects on the consolidation kinetics upon adding a polyamine hardener, and on the final properties of consolidated parts. With the isoelectric point of the naked particle surface decreasing, there were noticeable decreases in gelation time, shrinkage, green density, and flexural strength of the green ceramic body's properties. An interaction model is proposed to explain the observed differences. The potential of EGC to consolidate ceramic microneedles cast in soft rubber moulds was demonstrated.

1. Introduction

Epoxy Gel Gasting (EGC) was recently proposed as a suitable direct consolidation technique to fabricate high green strength micro-components by casting suspensions into silicon rubber moulds [1–5]. Micron size multifunctional components are valuable for advanced applications such as in microelectromechanical systems (MEMS) and biomedical devices (Bio-MEMS). High green strength to overcome the elevated shear stresses upon unmoulding is an essential requirement, especially when envisaging micro-components with high aspect and surface to volume ratios. The traditional Gel Casting (GC) based on the *in situ* polymerization of monomers and dimmers [6] revealed to be completely unsuccessful in conferring the necessary green strength to PZT pillar arrays, which systematically broke upon striping them from the silicon rubber molds. Contrarily, EGC was successfully applied to the fabrication of different kinds of micro-components, including pillar arrays for piezoelectric micro-transducers from aqueous suspensions of PZT [1,2] and barium strontium titanate [3,4]. The micro-sized parts kept integrity making EGC a potential alternative fabrication technique to replace the time consuming and technologically demanding micromachining approaches. The suitability of EGC to consolidate larger size components had already been consolidated based on the amine induced curing of ceramic slurries [7–9]. Therefore, EGC is the most well suited casting technology to fabricate a large variety of multifunctional microcomponents, such as ceramic microneedles.

Like in any other colloidal shaping technique, the intrinsic quality of ceramics produced by EGC is mostly determined by the suspension features [1,10–13]. Low viscous and high concentrated suspensions are mandatory to obtain a good compromise between good flowing upon casting and undergoing small shrinkages upon drying and sintering. The importance of this balance is particularly emphasized in the case of micro fabrication due to the rising dif-

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ficulty in filling and subsequently de-molding components having micro-features lower than 10 μm in size. The mechanical integrity of the green and subsequent sintered parts depends essentially on a well-balanced formulation of the suspension containing optimized proportions of epoxy resin, dispersant, ceramic powder with a suitable particle size distribution, and hardener [1–4,6–8,14,15]. All these components need to be compatible and achieve a high degree of homogeneity, making a ceramic suspension for EGC a quite complex system.

The properties of simple ceramic suspensions are mediated by the attractive and repulsive forces among the particles [10,13,16]. For an effective dispersion of ceramic powders in aqueous suspensions, several critical factors need to be considered including pH, [17,18] surface chemistry of powders, [19] and how it interacts with the dispersing agent [20–22]. The role of each relevant factor needs to be well understood and controlled. Usually, there is an optimum amount of dispersant and an optimum pH range for producing concentrated slurries of a given powder [23–25]. When other components (epoxy resin and hardener) are added to an EGC suspension, the specific interactions of these additives with the surface of the particles are likely to change with the surface chemistry of powders and need to be considered either. The specific adsorptions of the epoxy resin molecules having a slightly cationic character relative to the isoelectric point of solid PZT particles fostered a more extensive subsequent adsorption of the anionic dispersant, thus enhancing the overall dispersing degree of the EGC system [1]. But the consequences of the specific interactions between the processing additives used in EGC and the surface of the particles in terms of curing kinetics and physical properties of the green components was not disclosed so far [3,4,6–8,10,13,14].

In the present work, three ceramic powders (fused silica, zirconia and alumina) with different surface chemistries were adopted for preparing concentrated suspensions for EGC. The aim is to clarify how the specific interactions between the surface of the particles, dispersants and epoxy resin affect the kinetics and exothermicity of the cure reaction upon adding the hardener, and the physical properties of the consolidated green bodies. Ceramic microneedles were finally fabricated by EGC using micromoulding with powder suspensions presenting the best compromise in different essential steps: (i) adequate flowing during mould casting, (ii) time available for casting, (iii) high strength to guarantee safe de-moulding.

2. Experimental procedure

2.1. Materials and reagents

The selected ceramic powders with distinct isoelectric points were: Fused Silica (Min-SIl 200F, Minco, Midway, USA) with density = 2.2 g cm^{-3}, medium particle size = 28.8 μm and IEP around pH 2; Zirconia (3YS, TOSOH, Japan) with density = 6.05 g cm^{-3}, medium particle size = 0.48 μm and IEP around pH 4; and Alumina (CT3000, Alcoa Chemie GmbH, Ludwigshafen, Germany) with density = 3.98 g cm^{-3}, medium particle size = 0.57 μm and IEP around pH 9. Dolapix CE 64 (Zschimmer & Schwarz, Germany), an alkali free carboxylic acid based polyelectrolyte, was selected as anionic dispersant (D) for all ceramic powders. An epoxy resin (ER), ethylene glycol diglycidyl ether (Sigma–Aldrich, Germany, 1.152 g cm^{-3}) soluble in aqueous media and, a polyamine hardener (H), bis (3-aminopropyl) amine (Sigma–Aldrich, Germany, 0.958 g cm^{-3}) were employed as consolidating agents. The schematics of their chemical formulas and functional groups are displayed in Fig. 1. The opening of epoxy groups under certain environments (in the presence of amine groups or hydrated surfaces) is also sketched.

2.2. Suspensions preparation and characterization

Considering the importance of having similar average particle sizes and particle size distributions for all the tested powders, the coarse fused silica powder was attrition milled (AM) in aqueous media for 16 h up to obtaining a medium particle size close to that of alumina, followed by drying at for 24 h at 110 °C. Particle size distributions were determined by using laser particle size analyser (Coulter LS 230, Buckinghamshire, UK, Fraunhofer optical model). For comparison purposes, fixed concentrations of solids (45 vol.%) and dispersant (1 wt.% relative to dry mass of solids) were used for all the powders (fused silica, zirconia, alumina). Different amounts of ER were added (10, 15 and 20 wt.%, relative to the amount of water).

Zeta-potential measurements (Malvern Zeta sizer, Nano ZS, Malvern, Worcestershire, UK) were performed for all the powders in the absence and in the presence of dispersant and epoxy resin, using 1 mM KCl solution as background electrolyte. The pH adjustments were performed by adding 0.1 M solutions of either NaOH or HCl, to increase or decrease pH, respectively. The viscosity of suspensions was measured using a rotational rheometer (Kinexus, Pro+, Malvern, Worcestershire, UK) within the shear rate range of 0.1–500 s^{-1} using a cone and plate (4, 40 mm, gap 150 μm) measuring configuration. The gelation behaviour of the suspensions with different contents of ER and H was assessed with the same rheometer by measuring the evolution elastic (G') and loss (G") modulus under oscillatory mode. Time sweep tests were performed at a constant frequency of 1 Hz for durations up to 60 min by using plate–plate configuration (20 mm diameter). A fixed added amount of H (0.275 mL g^{-1} of ER) was used according to the manufacturer recommendations.

The exothermicity of the chemical interactions triggered upon mixing the different components of the EGC system were assessed using a temperature sensitive device (Fluke, 54 IIB, Type K thermocouple, Fluke corporation, US). Fixed aliquots (10 ml) of suspensions containing 45 vol.% solids (silica, zirconia, or alumina) and different amounts of resin (20, 15 and 10 wt.%, relative to the mass of water) were essayed at room temperature (RT ~20 °C). The suspension container was wrapped with an insulating apparatus to minimize thermal exchanges. The thermometer was inserted into the suspension and the monitoring of temperature started before adding the H. The required amount of H was then added under continuous stirring for 1 min while keeping temperature monitoring at each 30 s within the first 15 min, and then at each 2 – 5 min along the remaining 45 min (total monitoring time period of 1 h).

The total heat liberation might not derive only from the cure reaction of ER + H, but also from other specific chemical interactions between the surfaces of the powders particles and the processing additives. In an attempt to discriminate the type and the approximate intensity of such specific interactions, 10 ml of the following incomplete systems were also prepared: (i) an aqueous dispersant solution (corresponding to 1 wt.% relative to the dry mass of solids in a 45 vol.% slurry); (ii) a 45 vol.% silica slurry dispersed only in the dispersant solution; (iii) a 30 vol.% silica slurry dispersed in deionized water. A fixed amount of H (the one required for crosslinking the complete 45 vol.% solids loaded suspensions containing 20 wt.% of epoxy resin) was then sequentially added to all these systems and the evolution of temperature was monitored using the same apparatus and procedure described above for complete suspensions.

2.3. Characterization of green bodies

For mechanical characterization, green rectangular shaped bars (70 × 8 *x* 8 mm) were cast in silicone molds under partial vacuum conditions (21 kPa) and left there up to complete consolidation at room temperature (RT). After de-moulding, the green samples were

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