



Optimization of binder removal for ceramic microfabrication via polymer co-extrusion

Khurshida Sharmin, Ingmar Schoegl*

Department of Mechanical and Industrial Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

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Abstract

The objective of this study is to assess the feasibility of solvent extraction (SE) for partial binder removal in the context of polymer co-extrusion with a thermoplastic binder component. Polymer co-extrusion is able to produce multilayered, functionally graded and/or textured structures in an efficient manufacturing process, but requires a polymer binder system with suitable flow characteristics. Traditionally, the binder is removed by thermal debinding (TD), which, however, is prone to form cracks or blisters, both of which are attributed to a lack of initial pore space that allows pyrolysis products to escape. The primary focus of this work is to demonstrate that a binder system with a high soluble binder content is suitable for conventional polymer co-extrusion and to document that a two-step binder removal process involving both SE and TD eliminates debinding defects. The overall fabrication process is documented for the extrusion of solid ceramic rods and co-extrusion of tubes, where alumina powder was batched with polyethylene butyl acrylate (PEBA) as backbone polymer and polyethylene glycol (PEG) as water soluble binder. SE for specimen with varying PEBA:PEG ratios was tested in water at three different temperatures for various times. The 1:1 mixture showed a PEG removal up to 80 wt.% of the original PEG content after 6 h extraction; after subsequent thermal debinding, rods and tubes sintered successfully without defects, demonstrating the viability of the process.

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1. Introduction

Co-extrusion of thermoplastic compounds loaded with ceramic powders is a cost effective and promising method for manufacturing multilayered, functionally graded, or textured structures. By simultaneous extrusion of a feedrod assembled from multiple materials, diphasic or multilayered structures are easily fabricated. In the available literature, there are two different types of binder systems used for co-extrusion: (i) thermoplastic polymers [1–4] and (ii) waxes and/or starches [5,6], where in either case the binder system requires suitable rheological characteristics to achieve accurate shape reduction during co-extrusion. Thermoplastic binders facilitate the fabrication of intricate structures, and the construction of micron-scaled structures using multiple passes with

increasingly complex feedrods is well documented [1,2,4]. Most studies with thermoplastic binders, however, focus on the fabrication of green bodies: despite added complexity of the burn-out process, debinding and sintering steps are often not addressed in detail. Commonly used polymer binders include EVA (ethylene vinyl acetate) [2,7], EEA (ethylene ethyl acrylate) [1,8–10], PEBA (polyethylene butyl acrylate) [11–13], and LDPE (low density polyethylene) [14]. Due to the lack of a soluble binder component, the documented polymer binder mixtures require thermal debinding (TD) with exceedingly low heating rates and carefully selected heating schedules, as they are prone to form cracks or blisters during debinding [1,13,14].

Since the late 1990s, a range of studies have been conducted on microfabrication based on co-extrusion of ceramic materials using thermoplastic binder systems. The fabrication process involves three fundamental issues, (a) similar rheology for dissimilar materials to ensure successful extrusion, (b) binder removal without damaging the specimen, and (c) matched

*Corresponding author. Tel.: +1 2255784332.

E-mail addresses: ksharm5@tigers.lsu.edu (K. Sharmin), ischoegl@lsu.edu (I. Schoegl).

densification for co-sintering. Ismael et al. investigated the flow characteristics for co-extrusion and successfully done with the similar flow property between lead zirconate titanate/low density polyethylene (LDPE) and carbon/LDPE mixtures [14]. Xu and Hilmas studied the viscosity of pure polymer melts and ceramic/polymer mixtures for rheology control in the co-extrusion process [11]. In addition to binder systems that involve thermoplastic polymers, the importance of matched rheologies in the context of co-extrusion has been documented for conventional pastes [5,6]. Once co-extruded samples are obtained, conventional TD is commonly suggested for binder removal. In TD, the initial step involves the decomposition of polymeric additives into gaseous species [15], where non-trivial chemical interactions between mixture components have been documented [10]. Gaseous decomposition products formed in the interior of the sample have to diffuse to the sample surface. If the escaping rate from the sample is not sufficiently high, vapor nuclei are formed that grow into bubbles and result in bubbling and bloating [16–18]. Defects originating in the debinding process can be attributed to a lack of initial pore space for outgassing of pyrolysis products. Another source of defects is co-sintering of dissimilar materials, where a mismatch of sintering shrinkage percentages and sintering temperatures can cause slumping or interface instabilities [2].

Co-extrusion with thermoplastic binder systems involves batching of mixtures, construction of a feedrod, extrusion, debinding and sintering. A comparison to other ceramic forming technologies reveals some similarities to powder injection molding (PIM), despite having significant differences in the forming steps with associated differences in binder rheologies. In the context of PIM, debinding processes and elimination of debinding defects have been documented in detail. Using conventional TD, improvements have been achieved by controlling the debinding schedule and heating rate [19], using inert atmosphere to minimize the oxidation [17], placing samples on powdered bed to wick liquefied binders through interconnected pores [18] or using a low molecular weight binder with low boiling point to initiate pores at an early stage of TD [20]. As an alternative to TD, solvent extraction (SE) uses a binder component that is soluble and can be removed. Solvent extraction is a two-stage process consisting of dissolution and diffusion [21,22]. Once the samples are immersed in a suitable solvent, the soluble binders start to incorporate solvent into a swollen gel, which starts to dissolve once the solvent concentration is sufficiently large [23]. This partial removal of the binder creates pore space and as the debinding time increases, the pore spaces are expanding to the inner region of the samples. A combination of SE and TD has been proven to be an efficient approach to eliminate defects [19,24]. Pore space created during the initial SE step allows pyrolysis gases to escape during subsequent TD, and thus lead to a reduction of cracks [22,25]. Studies on combining SE using PEG as soluble binder with TD reported crack free samples [26,27] and reduced debinding times [19]. It has, however, been shown that cracks or blistering can be caused by swelling of PEG, especially at higher temperature

and for high molecular weights [28]. Zaky and Lin et. al reported the swelling effect at 60 °C for different binder systems (wax and SA) [29,30]. When different combinations of low and high molecular weight of PEG were used as soluble binders, it was observed that binders containing high molecular weight of PEG (6000, 8000) can cause the defects even at temperatures as low as 30 °C, 40 °C, and 50 °C [24,28]. Using low to medium molecular weight PEG (400, 600, 1000, 1500, 3350) as water soluble binders, no swelling was reported [26,27]. It was suggested that the combination of low and high molecular weight of PEG yielded no swelling effect up to 50 °C [24,31].

The present work seeks to demonstrate the feasibility of a combined SE/TD debinding process for a binder system that is suitable for polymer co-extrusion. A thermoplastic binder backbone (PEBA) and a water soluble binder component (PEG) are used for the extrusion of solid alumina rods and co-extrusion of alumina tubes. A conventional PEBA mixture without soluble components was used as a control. The combined SE/TD debinding process was investigated for varying PEBA:PEG ratios, solvent temperatures and debinding atmospheres. Defects were studied for both green and sintered specimen.

2. Experimental procedure

Ceramic rods and tubes with water soluble binder components were fabricated by (co-)extrusion. All results are documented for 5.84 mm diameter samples.

Materials and batching. Alpha alumina powder (Al_2O_3 , Informat Advanced Materials) with particle size 150 nm was used for all ceramic/binder mixtures. For the preparation of carbon cores for co-extrusion, carbon black BP 120 (Cabot Corporation) was used instead of alumina. The binder system consists of PEBA to maintain green strength, and PEG as water soluble binder. PEBA (Lotryl 35-BA-40, Arkema Inc.) is a random copolymer of ethylene and butyl acrylate containing 33–37% butyl acrylate with an overall melt index of 35–45. Two molecular weights of PEG were used in this work: PEG6000 (Alfa Aesar) as binder and PEG200 (J.T. Baker) as plasticizer. For the control mixture without soluble component, heavy mineral oil (HMO, Fisher Scientific) was used as a plasticizer.

All the binder materials were batched with ceramic powder in a HAAKE Rheocord 90 (Rheomix 600) at 30 rpm and 130 °C. The ceramic powder loading was 55 vol.% to ensure densification [11]. The volume of the mixing chamber with roller rotors was 69 cc and 70% of the volume was filled during mixing. For batching, half of the alumina powder and half of PEG6000 were added simultaneously to the molten PEBA. The remaining alumina powder and PEG6000 were added slowly; the viscosity was adjusted using PEG200 before kneading the mixture for 25 min. All batches were processed twice to ensure homogeneous mixing. Table 1 lists the mixture compositions prepared for this study, where the PEG amount increased while PEBA was reduced.

Extrusion. Extrusions and co-extrusions were performed with a custom ram extruder constructed from on a 30 KN ComTen

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