Fabrication and Characterization of Miniaturized Components Based on Extruded Ceramic-Filled Polymer Blends

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FABRICATION AND CHARACTERIZATION OF MINIATURIZED COMPONENTS BASED ON EXTRUDED CERAMIC-FILLED POLYMER BLENDS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Mechanical Engineering

by

Khurshida Sharmin
MS, Mechanical Engineering, Tuskegee University, USA, 2011
December 2015
Acknowledgments

I would like to express my sincere gratitude to Dr. Ingmar Schoegl, my advisor, for his excellent guidance, assistance, invaluable suggestions and inspiration on the all aspects throughout my PhD study at Louisiana State University. Without his help and support, this dissertation would not have been possible.

I would like to thank Dr. Ioan Negulescu for giving access to a torque rheometer for mixture batch- ing, Dr. Rafael Cueto for assistance with TGA, and Dr. Shengmin Guo for giving access to a sintering furnace. I am also thankful to Dr. Desiderio Kovar and Dr. James Mikulak at UT Austin provided critical insights for the extrusion process. I also thank undergraduate students Darria Carter, Tyler Lollis, Antony Pisano, Marcus Vasquez for assistance in batch mixing. In addition, Cabot corporation, Arkema Inc., and Corning Inc. are acknowledged for providing materials.

The assistantship partially offered by the LSU/CoE Fund for Innovation in Energy Research (FIER) is fully acknowledged. I also wish to acknowledge the LSU/CoE Fund of Chevron Innovative Research Support (CIRS) for funding support. I also want to thank Dr. Dimitris Nikitopolous and Dr. Daniel Park for their help in the collaboration work for ceramic embossing.

I would also like to thank my committee members Dr. Dimitris Nikitopolous, Dr. Shengmin Guo, Dr. Sunggook Park and Dr. Gregory L Griffin for evaluating and valuing my research work. Special thanks to the faculty, staff and fellow students at Department of Mechanical and Industrial Engineering, Louisiana State University who assisted me in my research.

I would like to thank Avishek Guha, Mohsen Ayoobi, Mandeep Sharma, Pawan Sharma in our research group and friends and colleagues for their help. Most of all, I am really grateful to my lovely family, my parents and my husband Mohammad Washim Dewan, who have always been beside me throughout of this work.
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Abstract

The objective of this work is to develop an improved manufacturing process for microstructured ceramic components that is based on co-extrusion. Co-extrusion of structured feedrods holds promise for development of multi-layered, functionally graded and/or textured structures. However, it requires a polymer binder that is difficult to remove before structures can be sintered to full density. A two-step debinding is introduced to eliminate debinding defects that are commonly observed in thermal debinding (TD). Cracking is a major issue due to a lack of pore spaces for outgassing of pyrolysis products in traditional TD. In two-step debinding, a soluble binder is removed partially by solvent extraction (SE) which creates a porous network and allows gases to escape in subsequent TD of remaining binder components.

The feasibility of solvent extraction (SE) 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 specimens with varying PEBA:PEG ratios were tested in water at three different temperatures for various times. Experiments were also performed with different grades of PEBA and EVA to investigate the effect of thermoplastics on SE. The 1:1 mixture showed a PEG removal up to 80wt.% of the original PEG content after 6h extraction. After subsequent thermal debinding, rods and tubes were sintered successfully without defects, demonstrating the viability of the process. Scanning electron microscopy and optical analysis were performed to characterize the process.

In order to illustrate potential applications, microfluidic devices were manufactured using extrusion followed by hot embossing. Ceramic microfabricated components have advantages over silicon, glass or polymer devices in terms of their ability to sustain high temperatures without compromising their functional capabilities. Flat tapes were extruded to create substrates, which were subsequently embossing micro patterns using a brass metal mold. To seal the microchanneled feature, a glass slide was attached to the chip by thermal bonding. Though a good bond was obtained, small portions were found where poor bonding was observed. To check leakage, colored water was forced to flow through the channel, and no leakage of water was found. A low temperature sintered ceramic material was fabricated as a potential alternative to the commercial low temperature co-fired ceramic (LTCC) tape. Overall, the study describes new possibilities for microstructure fabrication on ceramic based substrate and established the
embossing process as a promising technique for fabrication.
Chapter 1
Introduction and Literature Review

The research work presented here is an investigation on fabrication method of ceramic microstructures based on co-extrusion and embossing. The development of the whole process, starts with feedstock batching and rheological characterization, followed by two-step debinding, sintering, and the final properties are described for the manufacturing by co-extrusion. Hot embossing is studied as an approach to fabricate micro patterned features on ceramic materials for microfluidic applications.

Ceramic forming technologies include dry pressing or casting, powder injection molding (PIM), compression molding, extrusion and co-extrusion processes. Powder injection molding (PIM) is an economical shaping method to produce dense, small and complex parts [17]. This is a combination process of conventional powder technology and plastics injection molding. It is commonly referred to as metal injection molding process (MIM) or ceramic injection molding process (CIM), depending on whether metal or ceramic is used. However, conventional metals and ceramics processing techniques cannot compete with injection molding in terms of cost-effectiveness.

The problem with die casting is that it is not a continuous process, thereby limiting the quantity and the production time [18, 19]. In this case, extrusion (co-extrusion) allows a more efficient continuous production. Co-extrusion was found to be very useful to fabricate small-diameter tubes even at sub-millimeter scales [20] and is a possible technique for the fabrication of complex micro sized structures of ceramic and metal [3].

In ceramic processing, ceramic powder is mixed with a blend of polymer binders to form the “feedstock” mixture. The role of the binder is to hold the particles together while forming the shape and provide the ability to flow. In addition, it also provides strength of the green part. After shaping the part, the binder needs to be removed in the debinding step by either one or the sequential combination of some procedures including solvent extraction (SE), thermal debinding (TD), or catalytic cracking. Once the binder is completely removed, the particles are joined together by sintering. The main difference between co-extrusion and PIM lies in the forming process, where different binder systems are used. In this work, the fabrication of ceramics via co-extrusion or hot embossing involves four steps:
Co-extrusion is a process of passing two or more materials through the same die to produce a single piece; it involves repeated extrusion process. It has opened up a new generation in material engineering and addressed some previously difficult manufacturing needs. Figure 1.1 shows examples of ceramic microstructures by Van hoy and Greenwood group (left image) [21, 22] and complex honeycomb structures by Walker et al. (right image) [23]. A schematic illustration for feedrod fabrication steps of fibrous monoliths is shown in Figure 1.2 [1].

1.1 Motivation

Polymer co-extrusion is able to produce multilayered, functionally graded and/or textured structures in an efficient manufacturing process. Co-extrusion has been successfully applied in manufacturing of fine scale bi-phase microstructures [24], thin tube wall for SOFC electrolytes [25], ceramic honeycombs testing in thermochemical reactors [23]. Among the four steps, debinding is the critical step which involves the decomposition of polymeric additives into gaseous species [26] in the interior of the sample. These gases 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 [5, 27, 28].
Defects originating in the debinding process can be attributed to a lack of initial pore space for the outgassing of pyrolysis products.

Most studies with thermoplastic binder co-extrusions focus on the fabrication of green bodies: despite the complexity of the burn-out process, debinding and sintering steps are often not addressed in detail [3, 20, 21, 22, 23]. In the context of other ceramic forming technologies, powder injection molding (PIM), hot pressed or ceramic injection molding (CIM), debinding processes, and elimination of debinding defects have been well documented. Using conventional TD, improvements have been achieved by controlling the debinding schedule and heating rate [10], using inert atmosphere to minimize the oxidation [28], placing samples on a powdered bed to wick liquefied binders through interconnected pores [5], or using a low molecular weight binder with low boiling point to initiate pores at an early stage of TD [29]. Solvent extraction (SE) is an alternative to TD, it uses a binder component that is soluble and can be removed, which results in a porous network and prevents crack formations [30, 31]. In co-extrusion, there are three main difficulties: (i) co-extrusion of dissimilar materials requires matched rheological properties, (ii) debinding is required to remove the binder system without damaging the specimen, and (iii) co-sintering requires matched densification processes.

Hot embossing is an alternative forming technique for fabrication of micro patterned structures. Microstructured ceramic features have applications in biotechnology, sensor technology, chemical microreaction technique, and micro fluidic characterization. In this case, hot embossing offers a promising, cost effective method to generate micro structures on the surfaces of green substrate [15, 32, 33]. No study was reported yet on microfabrication of fabricated ceramic materials.
Figure 1.3: Methodology of binder removal and application

The present work seeks to demonstrate the feasibility of a combined SE/TD debinding for a binder system to remove debinding defects for polymer co-extrusion, as it is a cost effective and continuous process for multilayered, tubular or textured structures; hot embossing has been selected as an example for fabrication of micro patterns. Alternative fabrication pathways are less suitable: ceramics produced by pressing or casting are not dimensionally accurate and need machining. PIM is effective for high volume production, but is not suited for multilayered or tubular structures. Regarding micro patterns hot embossing is also offering a cost effective and more simpler way to manufacture micro features on ceramic.

1.2 Objective and Approach

The objective of this work is to develop a fabrication process for ceramic microstructures. A two-step debinding is applied to extrusion to address debinding defect issues. A combination of SE and TD has been proven to be an efficient approach to eliminate defects for PIM process [10, 17]. The main challenge is to investigate the feasibility of the combined SE/TD debinding for a binder system that is suitable for polymer co-extrusion. To describe a potential application, hot embossing is used to fabricate a ceramic microfluidic device.

A thermoplastic backbone binder and a water soluble binder component, polyethylene glycol (PEG), are used for the extrusion of solid alumina rods and co-extrusion of alumina tubes. A conventional polyethylene butyl acrylate (PEBA) mixture without soluble components is used as a control. The polymeric binders and feedstocks are studied in a variety of aspects, including compounding, rheological behavior, solvent debinding for varying binders, PEG ratios, thermal debinding and sintered microstruc-
Debinding studies are also performed to evaluate the effect of temperature, time, and atmosphere on binder compositions. Five different thermoplastic binders are used based on PEBA and ethylene vinyl acetate (EVA) to describe the effects of binder on debinding studies. It is expected that these features in Figure 1.3 Part I can explain the two-step debinding. This debinding technique is characterized on co-extrusion process to evaluate its adequacy (Fig. 1.3 Part II). To illustrate a potential application, hot embossing has been chosen to fabricate microfluidic devices due to its low cost and simple operation.

1.3 Literature Review

1.3.1 Existing Binder Systems for PIM and Co-extrusion

Binder systems have a major role in ceramic processing. Successful production of ceramic parts depends on the interaction and homogeneity of the feedstock mixture. The binder has an effect on the viscosity of the feedstock by forming for proper fluidity and properties of the final sintered structure. The binder acts as a temporary vehicle for forming the feedstock; after forming, it needs to be removed before sintering.

Generally, two binders are used: the backbone binder is usually a thermoplastic polymer that provides support and maintains the shape; the second binder improves the rheology of the feedstock. The second binder usually has low melting point and degrades very early in TD [29] or dissolves in solvent [30, 34, 35].

• 1.3.1.1 Binders used for PIM

Several polymers that have been used in PIM as major backbone binders are polyethylene wax (PW) [30], ethylene vinyl acetate (EVA) [36], polymethyl methacrylate (PMMA) [17, 37], high density polyethylene...
Zhou and Huang et al. studied binder systems using a low molecular weight binder with low boiling point to initiate pores at an early stage of TD [29]. Trunec et al. also studied the thermal removal of LMW binder in the initial stage and the effect of binder removal [36]. After removing the LMW binder, they found non-uniform binder distribution and defects in the sample.

A binder system with HDPE, PW and stearic acid (SA) was proposed by Thomas et al.; PW was soluble in heptane and HDPE was insoluble [10]. This is the first group who used HDPE for a PIM process and a good homogeneity with ceramic powder and moldability was reported. HDPE allowed working at a lower temperature that avoided the risk of decomposition of wax.

Yang et al. investigated the solvent debinding mechanism based on water extraction of a multi-component PEG binder system [30]. Solvent molecules diffused into the body and produced a swollen gel. When the amount of water was increased within the sample, PEG started to dissolve and diffused out.

A new binder system was proposed by Song et al. adding PMMA to the cellulose butyrate (CAB)/PEG binder system to improve the green strength [37]. Xianfeng et al. introduced a binder system with PMMA for fabricating parts from PIM process [17]. The binder proposed consists of at least two PEG components of different molecular weights, one of high molecular weight (HMW) and the other of LMW to avoid the leaching defects (Section 1.3.4). Backbone binder contents with higher than 20wt.% can reduce the stress from swelling.

**1.3.1.2 Binders for Co-extrusion Process**

In polymer co-extrusion, commonly used thermoplastic binder systems include EVA [21], ethylene ethyl acetate (EEA) [3, 20, 39], polyvinyl alcohol (PVA) [22], PEBA [23] or low density polyethylene (LDPE) [40]. Most of the available studies on polymer co-extrusion focus on the aspect of microfabrication, where details on the debinding process are often not reported.

EVA has shown favorable extrusion characteristics, where fine-scale ceramic objects with feature thicknesses as small as 10μm were formed (Fig. 1.4) [2, 21]. Hoy et al. fabricated microstructured ceramic objects with a binder system consisting of EVA as the binder and methoxypolyethylene glycol as the plasticizer [21]. Co-extrusions were repeated for four times without any significant defects where
the size of the forth stage is micron level. In another example, a 27mm scaled multitubular SOFC containing 61 cells were successfully prepared by multipass extrusion process [2]. From the optical and SEM images, it showed integrity after extrusion and uniformity between different anodes, cathodes, and electrolyte layers in green bodies.

EEA was used as binder with hydroxyapatite (HA) to fabricate macrochannels by co-extrusion and the final sintered part contained a uniform array of 270μm diameter, smooth pore channels [39]. Sun et al. also fabricated SOFC structures using EEA as binder material with Nio/YSZ [20]. In Figure 1.5, it shows an extruded body up to three stage co-extrusion done by Crumm and Halloran group [3].

Other binder systems with PVA were used to make alumina fiber strands [22]. By repeating extrusion stages, 3600 10μm fibers were separated by a thin layer of starch in 2.5mm by 2.5mm area. Small smearing and deformation were observed after co-extrusion.

In recent years, PEBA has became a common choice for studies on polymer co-extrusion [23, 41, 42]. A honeycomb ceramic structure was developed using PEBA and heavy mineral oil as binders based on polymer co-extrusion for thermochemical reactions [23]. Although they co-extruded and tested successfully, it showed slight distortions in the cell arrangement.
1.3.2 **Binder Characteristics and Rheology**

The rheological behavior of the binder system during co-extrusion is of fundamental importance [41, 42]. Controlling the relative viscosities is vital in eliminating or controlling detrimental defects found during the co-extrusion process. The materials are usually batched in a high-shear roller cone mixer or in torque rheometers, such as HAAKE Brabender [41] etc. This provides some measurable information on flow properties of polymers, structural changes during processing, and the influence of various additives on the processability of formulations.

An understanding of the rheology of each binder system is important in complex multilayer structures. Ismael et al. published a series of works on the investigation of flow characteristics for co-extrusion for a range of shear rates, and successfully done with the similar flow property between lead zirconate titanate/ low density polyethylene (LDPE) and carbon/LDPE mixtures [4, 40, 43]. They considered that the measured torque is proportional to shear stress and the roller speed is proportional to the shear rate; and apparent viscosity is the ratio of stress and shear rate to attain similar viscosity. This is the most significant step for co-extrusion [4]. The proportionality constants are dependent on geometric dimensions of the rheometer [44, 45]. Using the apparent viscosity vs roller speed plot, the viscosity from torque rheometer data was matched and validated for co-extrusion tests (Fig. 1.6).

Xu and Hilmas studied the viscosity of pure polymer melts and ceramic/polymer mixtures for rheology control in the co-extrusion process [41]. Rheological behavior of Al₂O₃ and ZrO₂ pastes were
characterized using a capillary rheometer by Kaya et al.[24]. They used the Benbow–Bridgwater relationship (Eq. 1.1). In addition, Greenwood et. al co-extruded alumina fibers and starch with similar viscosity behavior [22].

\[ P = 2\ln\left(\frac{D_0}{D}\right)(\sigma + \alpha V^m) + 4\left(\frac{L}{D}\right)(\tau + \beta V^m) \]  

(1.1)

where \( P \) is the pressure, \( D_0 \) and \( D \) are the diameters of the barrel and the die, respectively, \( L \) is the length of the die land, \( V \) is the extrusion velocity, \( \sigma \) is the die entry yield stress, \( \tau \) the die wall shear stress; and \( \alpha \) is the die entry, \( \beta \) is the die land velocity coefficients and \( m \) and \( n \) are the die entry and die land velocity exponents, respectively.

Due to the irregular shape of the roller, rheological data interpretation is difficult with using only torque rheometer data. Viscosity and shear rate data cannot be measured directly from the torque rheometer. Some studies have been performed on modeling work to convert the data from torque rheometer to viscosity data [44, 46]. Goodrich and Porter calibrated the torque rheometer for newtonian fluids assuming the chamber being equivalent to two co-axial cylinders [44]. Another group, Blyler and Daane, studied this relationship for non-newtonian fluids and tried to determine the shear rate distribution on the roller (Eq. 1.2) [46]. Although this approach is dependent on capillary rheometer data for constant \( K \), it concludes that the slope from log(torque) vs log(roller speed) from torque rheometer is identical to the slope of the log(viscosity) vs log(shear rate) plot from the capillary rheometer.

\[ M = C(n).K.N^n \]  

(1.2)

Here, \( M \) is the measured torque, \( N \) is the roller speed and \( C(n) \) and \( K \) are constants.

Bousmina et al. suggested a universal quantity (Eq. 1.3) independent to the nature of fluids and rheological properties [47].

\[ Ri = \frac{R_C}{\left[ 1 + \frac{4\pi N}{n} \left( 2\pi M L R_C^2 \frac{1 + \frac{\beta}{\alpha} \gamma^{n+1}}{M} \right)^\frac{1}{2} \right]^\frac{1}{2}} \]  

(1.3)

where \( R_C \) is the radius of the mixing chamber, \( M \) is the torque exerted on the roller shaft, \( g \) is the gear
ratio, \( N \) is the roller rotational speed per second, \( n \) is the power law index, \( m \) is the melt consistency index, and \( L \) is the roller length.

However Xu and Hilmas found a large deviation using the Bousmina model for ceramic/polymer mixture [41].

### 1.3.3 Defect Formation During Debinding

Binder burn-out is a process performed before sintering, where a green sample is heated until the polymer binder is decomposed and escaped from the sample. It is the step of removing binders by thermal treatment (called binder burn-out). Debinding is considered a critical step for the successful production of ceramic parts, where green bodies are formed using ceramic-filled thermoplastic binders [5, 28]. In published literature on co-extrusion, conventional thermal debinding has been the method of choice for binder removal, although it is prone to create debinding defects when applied to thermoplastic binders. In TD, the initial step involves the decomposition of polymer additives into gaseous species (acetic acids from EVA, butane from PEBA polymers) [26] where these 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 bubbling and bloating are happened for PIM [5, 28]. Defects originating in the debinding process can be attributed to a lack of initial pore space for the out gassing of pyrolysis products.

Hrdina and Holloran studied defects on moldable ceramic system for EVA binders and confirmed that defects originated from the binder degradation [27, 48]. EVA is rather labile during thermal decomposition, where formation of acetic acid vapor as a decomposition product starts at temperature below 200°C [26]. It was required to diffuse to the surface, otherwise bubbles are formed when a critical pressure level is exceeded [27, 48].

Alternative debinding techniques have found much larger interest in the context of PIM. In order to reduce burn-out defects, the following approaches have been studied on using only thermal debinding: controlling the debinding schedule and heating rate [5, 10], inert atmosphere [28], and placing the sample on a bed of wicking powder [5]. Figure 1.7 shows the cracking defects found during TD at a higher heating rate for a wax based zirconia system [5]. Trunec et al. investigated the effect of TD atmospheres - air, oxygen, nitrogen, carbon dioxide and vacuum, and the heating rate on binder removal [28]. Defect
free specimens were found under nitrogen and carbon dioxide atmospheres at a heating rate of 10°C/min. Increasing the heating rate to 15°C/min, cracks were created at the center due to the faster debinding cycle. Binder removal in air and oxygen even at a lower heating rate of 3°C/min showed bloating and cracks due to faster oxidation. In the documented literature, polymer binder mixtures require TD with exceedingly low heating rates and carefully selected heating schedules.

In PIM, combining solvent debinding with thermal debinding was the most promising technique to eliminate defects [10, 17, 31]. Leaching or extraction of one binder component created porosity in green parts. In subsequent thermal debinding, these pore channels allowed pyrolysis products to escape and thus lead to a reduction of cracks [30, 31].

In the area of co-extrusion studies have used alternative binder systems, where considerable efforts were directed towards an improved understanding of interactions between constituents of binder systems during thermal debinding [49, 50]. In comparison to EVA, PEBA is relatively stable at pyrolysis conditions [26], which results in a less rapid decomposition during TD. Nevertheless, ramping rates as low as 2 – 3°C/h over a wide range of temperatures were recommended in a recent study [23]. Exceedingly slow debinding schedules in conventional TD hinted at the importance of slow out gassing of volatile products to prevent debinding defects.

1.3.4 Solvent Extraction

Solvent debinding involves the extraction of partially soluble binders of low molecular weight in the dense body by solvent evaporation–condensation, solvent immersion, and super critical extraction. A part of the solvent binder system is soluble and can be removed. This partial removal of the binder
creates pore spaces and as the debinding time increases, the pore spaces are expanding to the inner region of samples. Dissolution and diffusion phases are found in solvent extraction [11, 30]. Once the samples are immersed in a suitable solvent, the soluble binders start to incorporate solvent into a swollen gel and when the solvent concentration is sufficiently large, it starts to dissolve [51].

Zaky et al. tested several SE variables on the shape maintenance on the green 17-4PH metal body for PIM [35]. The binders included EVA/paraffin wax/stearic acid, where wax was dissolved in organic solvents (n-heptane, n-hexane and iso-octane). Authors studied the extraction temperature, time and solvent feed ratio to dilution.

Vielma et al. demonstrated the technique for solvent extraction in n-heptane with thermal debinding for PIM and reduced the debinding time as well as the crack formation [10].

Many experimental and theoretical investigations have been done on the solvent extraction for (PIM) [10, 34, 37]. Tsai and Chen described the solvent binder removal along radial positions for PIM using a single parameter model [34]. Samples are extracted in n-hexane, n-heptane and n-octane at three temperatures of 50, 60 and 80°C and measured the extracted weight by TGA at different positions from the surface to the center. However, this model failed to correlate at lower leaching time and found a source of error at the interface of the core (where wax remained) and shell (where wax removed) area.
Debinding mechanism for a CIM part was investigated by Krauss et al. [6] and a model with the shrinking core model was proposed to find an effective diffusivity. The experimental data points had a good agreement with this model and confirmed that solvent extraction is a diffusion controlled process (Fig. 1.8).

Zhu et al. described the condensed solvent debinding for slab, sphere and cylindrical shapes. Heptane was used to create solvent vapor and condensed on samples surface where binder was removed by the interdiffusion of binder and solvent.

Some authors also worked on variables that were affecting the shape and dimension of the sample with solvent debinding time [7, 52]. A length scale was developed to explain the binder removal behavior for two different shapes considering the debinding from the component along all three directions [7], shown in Figure 1.9. In another study, Oliviera et al. studied the debinding mechanism for the ratio of surface area to volume [52]. They found samples with higher surface area to volume ratios require less time due to larger solvent accessibility to soluble components.

Due to the unfavorable effects of organic solvents to operators and the environment, studies have focused on other binder systems including PEG as water soluble binders [17, 19, 37, 53]. Water debinding is a requirement once it a has lower environmental impact, is economically attractive, and is less
hazardous than the conventional catalytic or organic solvent debinding. It has been shown, however, that cracks or blisterings can be caused by swelling of PEG, especially at higher temperatures and for high molecular weights [37, 54]. When different combinations of low and high molecular weights 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 low temperatures of 30°C, 40°C, and 50°C [17, 37]. Zaky and Lin et al. also reported the swelling at 60°C for different binder systems (wax and SA) [35, 54]. Using low molecular weight of PEG (400, 600, 1000, 1500, 3350) as water soluble binders, no swelling was reported [19, 53]. Xianfeng et al. suggested the combination of low and high molecular weight of PEG yielded no swelling up to 50°C [17].

1.3.5 Thermal Debinding

There are several factors for thermal debinding to get a defect free object: heating rate, holding time, highest temperature, atmosphere. Studies have been done to investigate defects originating from thermal debinding [5, 28, 36, 48]. Higher heating rates can cause microcracks in the green body [10, 31], because decomposed gases do not get enough time to diffuse out from the sample. Binder burn-out rates must be controlled. Trunec et al. studied the atmospheric effect on the burn-out process for alumina with the EVA binder and found cracks in vacuum, air and carbon dioxide medium [28]. Defects formation during TD is explained in Section 1.3.3.

1.3.6 Sintering

Sintering is a firing process by which a system of particles reaches a maximum densified state. Densification is the act of reducing porosity of the sample, therefore may be making it denser. Sintering can be divided into two categories - solid state sintering and liquid phase sintering. A pure, single phase, polycrystalline material is densified by solid state sintering where materials are heated between 50% and 80% of the melting point.

Sintering is occurred by matter diffusion in the solid state. There are 6 different mechanisms for sintering process (Fig. 1.10).

1. Surface diffusion
2. Lattice diffusion from the surface
3. Vapor transport
Figure 1.10: A schematic representation of sintering mechanism of two particles

Figure 1.11: Sintering phenomenon for neck growth
4. Grain boundary (GB) diffusion
5. Lattice diffusion from GB and

All 6 are needed to bond and grow the necks between particles. Particles do not melt here, these stick to each other by neck growth (Fig. 1.11). Neck growth is preceded by the first 3 mechanisms; no densification is started during neck growth. Grain boundary (GB) diffusion and lattice diffusion are the most important densifying mechanisms. Plastic flow is responsible for both neck growth and densification, but is found in metal sintering.

There are three stages for solid state sintering mechanisms- the initial stage, the intermediate stage, and the final stage [55]. During the initial stage, surface curvature removes and forms concave necks between particles by diffusion and vapor transport. In this stage, 3-5% of linear shrinkage (65% relative density) occurred. The intermediate stage starts when 65% relative density is reached. Here microstructures look like a 3D solid network with continuous pores existing in the grain boundary. This stage covers the major part of densification (65-90% of relative density). In the final stage, pores are isolated in the network eliminated by continuously shrinking. The properties of densified object are dependent on the microstructures, pore distribution, pore sizes and grain growth. Both grains and pores sizes are increasing to enhance the densification, defined as coarsening. If the change of grain growth is in a narrow range, it is called normal grain growth. Sometimes few grains are increasing very quickly compared to surrounding grains, it is called abnormal grain growth. Grain growth is very important to obtain desired properties of object. Abnormal grain growth increases the diffusion distance, which slows down the densification process. Many studies are performed to get a densified structure where the sintering behavior, microstructures and mechanical properties are very important [18, 56]. A source of the defect is co-sintering of dissimilar materials, where a mismatch of sintering shrinkage and sintering temperatures can cause lumping or interface instabilities [21, 24].

Sometimes the solid state sintering temperature is too high to fabricate objects. In this case, addition of small amounts of liquid phase provides a higher diffusivity path for transporting matter and aids the sintering process [8, 57, 58], this is called liquid phase sintering. Figure 1.11 shows a model for liquid phase sintering for glass-ceramic sintering. In solid state sintering, grain boundary diffusion is the
Figure 1.12: Schematic of sintering model for glass-ceramic system [8]

parameter that controls the diffusion; it is a product of the diffusion coefficient and the grain boundary thickness. In liquid phase sintering, it is a product of the diffusion coefficient and the thickness of liquid layer. The thickness of the liquid layer is much greater than the grain boundary thickness, provided an enhanced matter transport. Good wetting of the solid by liquid is a significant parameter required for liquid phase sintering. Liquids with low surface tension have a good wetting of solid; while liquids with high surface tension show poor wetting.

Like solid state sintering, it also has three stages; rearrangement of particle and liquid distribution, solution-precipitation, and final densification [55]. At the softening temperature of liquid additives, liquid phase is formed and flows to different positions due to the pressure gradients. It wets the solid particles with liquid melt and particles can rearrange easily in liquid. Distribution of liquid is important to achieve the required properties for sintered objects. If a sufficient amount of liquid is present, full density can be achieved at the rearrangement stage. If low amounts of liquid are present, two additional stages are required to attain full density. In the solution-precipitation stage, solid dissolves in solid-liquid boundaries, diffuses through the liquid and precipitates at the other site of particles. In the final stage, it is very slow because of large diffusion lengths and sintering is dominated by Ostwald ripening. Ostwald ripening is a process of dissolving small crystals and redeposition onto larger crystals.
1.3.6.1 Critical Powder Concentrations

The solid loading is a major factor that affects shrinkage, dimensional stability, and final density. Powder concentration are commonly characterized by solids fraction, which is the volumetric ratio of solids powder to the total volume of powder and binder. Critical solids fraction is the composition where the particles are tightly packed and all space between the particles is filled with the binder [59]. Low solid loading causes high viscosity and trapped air pockets result in difficulties during shaping, and cracking during debinding and sintering, as well as product with low density [59]. Figure 1.13 shows a typical curve of the mixture apparent density against solids fraction. The mixture density is calculated by:

\[ \rho_{mix} = \phi \rho_P + (1 - \phi) \rho_b \]  

(1.4)

where \( \phi \) is the solids fraction of powder and \( \rho_P \) and \( \rho_b \) are the densities of the powder and binder, respectively. At a certain solids fraction, the density would not follow the calculated line because the particles are in their closest packing condition and binders sufficiently exist to fill the spaces between the particles. Different volume percentages of alumina powder were batched depending on binder types and forming methods. For injection molding, 60vol% alumina with PP [52], 50vol.% and 56vol.% with EVA/wax binder system [36, 60] and 55vol% with PMMA binders [19] were used. Hilmas et al.
Walker et al. used 55vol% of ceramic powders as critical powder loadings with a PEBA binder system for the co-extrusion process [23, 41].

1.3.6.2 Sintering Temperature

Temperature has a significant effect on the density of the sintered part [10, 61]. Thomas et al. investigated the sintering temperature and time for the alumina/HDPE/wax binder system [10]. They sintered the specimen at 1500°C, 1550°C, 1600°C, and 1650°C. Figure 1.14 shows the effect of sintering temperature on the densification of final sintered objects (percent of sintered densities with respect to theoretical density). A good density was found at 1600°C and was about 99.6% of the relative density. Aminzare et al. studied the heating rate for alumina samples and found that increasing the heating rate decreased the grain size and density [18]. Due to the high heating rate it provides less time to grow the grains. Some distortions and cracking were reported for co-sintering due to the warping caused by sintering shrinkage [21, 24].

Achieving full densification (theoretical density) is very difficult. In Figure 1.15, micrographs of the sintered samples are shown at different sintering temperatures [11]. With increasing temperature and density, porosity decreases from 11–14 vol.% to 1–3 vol.%. This is attributed by grain growth and removing pores.
Figure 1.15: Microstructures of sintered samples at a) 1250°C for 60min, b) 1250°C for 120min, c) 1370°C for 60min, and d) 1370°C for 120min [11]
1.3.6.3 Particle Size

For successful sintering, particle size is an important parameter to consider. It is noted that during liquid phase sintering, fine ceramic particles hinder the flow of liquid. Hence using larger particle size of alumina (lower specific surface area), sintering density can be improved [57].

1.3.7 Forming

In this work, the fabrication of ceramic objects by co-extrusion was studied. The second forming process embossing was used to fabricate micropatterns on ceramic samples to fabricate microfluidic chips.

1.3.7.1 Microfluidic Applications

Microfluidics is the science and technology that deals with the miniaturized fluid flow inside micrometer-sized channels. To consider a microfluidic structure, one dimension has to be in the order of a micrometer or tens of micrometers. Microchanneled structures were developed due to the increasing demand in biochemical and life science applications [62]. Certainly, microfluidic devices have generated a large variety of new research and development topics. Currently, the field of microfluidics is the focus that requires a fabrication facility for the production of reliable devices.

Microfluidics technology has found many applications, mainly the following.

- Biomedical applications: Demand in this area is increasing because these allow the integration of
many medical tests on a single chip.

- **Cellomics:** Microchannels have the same characteristic size as biological cells. Microfluidic chips can allow easy manipulations and analysis of single cells. Anderson et al. reviewed microfluidics as cell analysis chips and proved that this is a very useful concept for cell analysis [63].

- **DNA separation:** Figure 1.16 shows a picture of microfluidic chip fabricated by hot embossing on PMMA, which was successfully used for DNA separation [12].

- **Oil recovery from subsurface reservoirs:** Due to the opaque nature of real porous media, artificial porous structures have been extensively used to investigate the fluid transport in subsurface area.

- **Protein crystallization:** Microfluidic devices allow the generation on a single chip of a large number of crystallization conditions (temperature, pH, humidity).

- **Environmental monitoring systems:** A low temperature co-fired ceramic (LTCC) -based microfluidic system for sensing traces of heavy metals in biological and environmental fluids has been studied by Gongora-Rubio et al. [8, 64].

- **Many other areas including drug screening, glucose tests and chemical microreactors.**

**Materials for Microfluidic Devices:** In microfluidic applications, choice of materials and fabrication processes are critical for successful production of the device. In the past two decades, many studies have been conducted to investigate microfluidic device fabrication and its application. The use of diverse materials for microfluidics chips such as silicon, glass, polymers, ceramics, and metal is currently possible because of the development of a range of processes, e.g. deposition and electrodeposition, etching, bonding, injection molding, embossing and soft lithography. In the early 1990s, the majority of microfluidic devices were made from silicon (derived from semi-conductor industry) [65, 66]. Glass is a very attractive material in microfluidic application [67, 68]. It was used due to its chemical stability and high resistance to mechanical stress, large optical transmission range, and high electrical insulation properties. UV lithography and etching were used to pattern on glass substrate [68] and successful sampling and separation of bovine serum albumin (BSA) and anti-BSA have been achieved by Lin et al. [67]. However, difficulties in micro processing, high cost of fabrication, and the material itself limited the usage of glass as a microfluidic device material.

Low cost manufacturing and ease of processing supported polymer materials advantageous over
glass or silicon [69]. Polymer materials have wide choice options. A variety of polymers are available—polystyrene (PS), polyethylene terephthalate glycol (PETG), polymethylmethacrylate (PMMA), polyvinylchloride (PVC), polystyrene, and polycarbonate (PC). Manufacturers of microfluidic devices can select suitable properties that fit their specific application. One of the most common thermoplastic polymers, Poly(methylmethacrylate) (PMMA), has been broadly studied as a substrate material for microfluidic chips for its ease of fabrication, low price, excellent optic transparency, and electric and mechanical properties [69, 70, 71]. Narasimhan et al. [71] and Martinova et al. [72] studied the fabrication process parameter in PMMA substrate and microchannels with a minimum feature size of 40μm in width have been successfully fabricated. Microfluidic devices on PMMA substrates have been used as a microcapillary electrophoresis (μ-CE) device for DNA separation and detection [2]. Another study on PMMA and PC fluidic chips and surface modification was reported for DNA application [70]. By fabricating microfluidic devices on plastic substrates, it becomes high throughput and high-resolution patterning. Major drawbacks of the polymer are their poor thermal and chemical stability [8, 73, 74, 75].

Due to these limitations, researchers started to consider alternative material for microfluidic applications. Ceramic or modified ceramic materials have shown large number of advantages over those manufactured in glass, silicon, or polymers. These advantages include chemical inertness, biocompatibility, high-temperature stability, mechanical strength, and three dimensional structuring ability [8, 15, 73, 76, 77]. Aura et al. proposed ORMOCER (modified ceramic) as a good replacement of polymers in microfluidic fabrication [75]. ORMOCER is a blend of inorganic (ceramic) and organic materials having combined properties of chemical and thermal stability, cross-linking capacity, polarity, hardness and optical behavior. Microchannels of 20μm width was fabricated by UV lithography and 5μm fabricated by UV- embossing. Favorable surface properties proved ORMOCER material is well suited for microfluidics.

**Fabrication Method for Microfluidic Device:** A variety of approaches have been established for rapid fabrication of micro fluidic chips, including UV lithography [67], imprinting [72], soft lithography [78], laser ablation, injection molding [79], and hot embossing [15, 32].

Soft lithography refers to a fabricating method for replicating structures using elastomeric stamps, molds, and conformable photomasks (specifically polydimethylsiloxane (PDMS)). It is called "soft" be-
cause it uses elastomeric materials, most notably PDMS. Soft lithography using PDMS offers several advantages, including low cost, fast processing, facile sealing and bonding to a number of different substrates and multilayer fabrication to create complex 3D systems [80]. It also has some limitations, most organic solvents are soluble in PDMS, which can limit the use to aqueous solutions. In addition, poor thermal conductivity and gas permeability of PDMS is not suitable for carrying out in-channel oxygen-sensitive polymerization reactions.

In laser ablation for the fabrication of plastic microfluidic devices, new microfluidic designs are easily programmed into the system. The disadvantage of laser ablation process is its inherent serial nature, which severely limits its throughput [80].

The McMornick group used injection molding to fabricate a microfluidic device on acrylic polymers [79]. Due to the complexity of the molding equipment and fabrication of the mold, injection molding is not an appropriate method for reliable and easy fabrication.

Hot embossing is a very straightforward method. It is the most commonly employed technique because of its flexibility, low-cost microfabrication and compatibility with mass production [15]. After fabricating a mold (master), master mold and substrate material are heated at the emboss temperature depending on the type of material (Fig. 1.17). The mold insert is pressed into polymer substrate with a
precisely controlled force. The mold insert and substrate sandwich is cooled and master mold is separated from substrate; this is the last step of embossing called demolding. Advantages of the hot embossing process are:

- Simple and easy process ability
- Cost effective
- High quality replication
- Short time fabrication

Fabricating the master mold is expensive, which is the only drawback of the embossing process.

1.3.7.2 LTCC

Recently, low temperature co-fired ceramics (LTCC) materials have found attention due to easy integration of sensing and actuating electrodes of precious metals (Au, Ag, Pd and Cu. T) [8, 73, 74]. LTCC materials benefit with rapid prototyping and 3D structural capability that allows for multilayer fabrication. LTCC green material is available in a flat tape format consisting of ceramic, glass and organic compounds by a different manufacturing company [13, 74]. The physical properties such as shrinkage, thermal coefficient expansion (TCE) or thermal conductivity and other electrical properties are varying with different manufacturers [74]. Green tape 951 from DuPont company has 13%, 13%, and 15% of shrinkage in the x, y, and z directions, respectively, while CT800 from Heraeus company has no shrinkage after sintering. Different fabrication methods are reported for LTCC microfluidic devices: hot embossing [15, 76, 81, 82, 83], micro roller embossing [33], and lamination/LTCC technology [74, 84]. These
processes for LTCC are described in Section 1.3.7.1. Most of these studies used commercially available LTCC tapes. Due to the thinness of the tapes, several are to be joined to get the required thickness.

There are several groups who worked on LTCC materials with LTCC processing technique. In LTCC technology, punching and laser treatment are the preferred techniques to make channels, grooves, and vias in green tapes (Fig. 1.18). Vias are filled with conducting inks of Au and Ag acting as interconnects across layers, and electrical conduction lines are formed by screen printing. The individual layers are then stacked and a pre-firing lamination step is performed to temporarily bind all of the layers. The laminated LTCC device is then sintered in a programmable furnace.

There was a problem with the lamination due to the sagging or deformation of the layers (Fig. 1.19). It was necessary to fill the cavities with temporary inserts to avoid shape deformation in the lamination process and sagging during sintering. Golonka et al. decreased the sagging by using sacrificial material, however carbon contamination was found during sintering [84]. Also, it needs a well-planned temperature profile for the burn-out process of sacrificial material. Another group, Shafique et al., used multiple steps for lamination and low pressure in each step as a progression way eliminating the use of sacrificial material [77]. The binding between layers were found to be poor due to lower pressure.
Double sided tape and hot melt adhesives were also used to avoid sagging or deformation between layers [85].

More studies reported on fabrication methods of borosilicate glass and ceramic samples [86, 58, 57]. Most of these studies investigated the properties of materials including dielectric property, density, sintering temperature and microstructure; no study was performed on microfabrication of glass-ceramic material. In this present work, glass powders were added with ceramic and polymer binders to formulate a LTCC material. It was found that adding glass to ceramic lowered the sintering temperature from 1600°C to below 1000°C. To illustrate its ability to pattern microstructures, microchannel structure was embossed on it.

- **1.3.7.3 Hot Embossing:**

The mold insert for hot embossing is fabricated in a number of ways: CNC machining for 100μm structure [87], LIGA technologies (LIGA consists of three processing steps- lithography, electroplating and molding) for few μms range feature [87], UV LIGA method for nickel molds [82], laser ablation on polymer with nickel electroplating [81], and hot embossing of metal molds [76].

It has been demonstrated that hot embossing is a suitable and flexible process for the fabrication of micro components on polymer [69, 70, 71, 78, 79, 88], ceramic and modified ceramic materials [15, 89, 32]. Good structural replication of microfluidic chips indicated that this is a very favorable method for the production of polymer microstructures. This embossing approach has been also described by Narasimhan et.al to emboss microchannels in PMMA substrate [71]. In recent years, Yeo et.al introduced a hot roller embossing method on a PMMA structure to improve the production yield for polymeric microfluidic devices [69]. To improve the hot embossing process, a positive temperature coefficient ceramic heater was used as an automated temperature control device and showed a great promise for PMMA microfluidic chip [88].

Ceramic structures with feature sizes less than 500μm were fabricated by embossing [89]. It was mentioned as a potentially cost effective and viable method for large scale fabrication.

Rabe et al. proposed hot embossing as an alternative method to generate micropatterns on LTCC surfaces [15]. They used hot embossing in combination with lamination by adhesive methods. It was proved that a complex feature can be embossed on green surfaces by optimizing parameters such as
embossing temperature, dwell time, and pressure (Fig. 1.20), though some defects were reported due to the lamination. Shan et al. reported a series of studies on micro embossing of LTCC including substrate preparation, embossing, debinding and co-firing [33, 32]. Investigations from these studies proved embossing as a promising method for fabricating ceramic based microstructures and devices.

Embossing is a very reliable technique for microfabrication on polymer and ceramic modified materials. As of right now, many approaches were conducted on polymer or LTCC material; however, no attempt was made to emboss on ceramic for microfluidic chips. In this study, embossing is used to fabricate microchips on ceramic substrates.

- **1.3.7.4 Capping:**

In order to complete microfluidic chips, microchannels have to be closed without clogging or damaging the channels of structure. This is a big challenge to achieving a defect-free, well-shaped and enclosed fluidic chip. Several methods have been reported for bonding microfluidic chips including thermal bonding [88], solvent bonding, and Lamination technique for LTCC [15] and adhesive bonding [14] etc.. Thermal bonding is the most common approach used for bonding. Wang et al. used PMMA sheets to cover PMMA microchips by thermal bonding at 110°C [88]. A microchip and a cover sheet were put between two glass plates, where the cover was attached to the heater to ensure direct heating. The bonded chip
was then allowed to cool slowly to room temperature.

The McMornick group used 2mm thick Mylar sheets coated with a thermally activated adhesive as a cover for PMMA microchips [79]. A poor bonding was found for the plastic chip. The uses of adhesives or intermediate layers can clog or block the channels, which may affect the chip performance.

In capping, it is imperative to closely match thermal expansion coefficients of the two materials to be bonded. Stjernstrom et al. proposed glass covers for a glass substrate using thermal bonding. They placed the substrate with the cover glass downwards in an oven at 630°C for 6 to 8h. Lin et al. also used glass-glass bonding by a fusion process at 580°C for 20 minutes at a ramping rate of 5°C/min. For LTCC material, Rabe at al. used alumina tape as a cover and adhesive was layered on the cover tape to laminate before sintering [15]. Cavities and irregularities were reported during the lamination and sintering stage. Opacity is a drawback for ceramic based microfluidic chips; the cover should be transparent to aid optical exposure. A transparent plastic cover such as PDMS or glass cover can be a solution for ceramic based chips. The substrate material can be made from ceramic or ceramic hybrid material and the cover which seals the channeled structure is made of transparent glass or PDMS.

For LTCC material, capping was done usually in the green state and then fired to achieve a complete sealed chip [15]. A technique for the bonding of LTCC substrates to PDMS has been reported by Malecha et al. [malecha2009PDMS]. Pawel et al. reported the integration of transparent glass windows into the LTCC substrate/microfluidic devices [90]. After sintering with the glass window, 20μm sagging was found..

1.4 Outline

Chapter 2 presents the material properties and binder compositions for co-extrusion and embossing. The detailed fabrication procedure with the developed two-step debinding process and characterization techniques are described in chapter three.

Chapter 3 focuses on the study of two-step debinding technique for the extrusion. Solvent debinding is studied in two configurations; one of them is the characterization of extracted samples in terms of shape retention, density, shrinkage and microstructures. Results after TD at different atmospheres and sintering are also shown. In the other configuration, effects of thermoplastic binders on the debinding process are investigated and co-extrusion tests were performed for selected EVA and PEBA blends.
Fabrication of microfluidic devices by embossing on ceramic-binder mixing and the characterization are provided in Chapter 4.

Experimental results of glass-ceramic materials for low temperature sintering are described in Chapter 5.

In chapter 6, final conclusions are made of this work and future work is discussed. Future work includes the fabrication of a real rock based 3D microfluidic chip using the ceramic microfabrication technique.
Chapter 2
Materials and Experimental Procedures

This chapter begins with the description of powders and binder systems including the composition and fabrication process. The characterization of binder feedstocks including rheology and extrusion is explained in detail. The two-step debinding process is described for all extruded binder systems. Characterization tests for optical and morphological properties are conducted in order to demonstrate their processability and quality of sintered objects. Details of the fabrication process for embossing on ceramic materials are also described.

2.1 Materials

2.1.1 Precursor Powders

Ceramic Powder: Alumina is one of the most cost effective and widely used materials in the area of engineering ceramics. In this work, commercially available alpha alumina powder (Al₂O₃) from Inframat Advanced Materials was used. Alpha phase alumina was chosen because of its favorable properties [18, 61]. Due to high hardness and good thermal properties, it was the subject in many studies on manufacturing processes [10], sintering techniques and microstructures [18]. In this work, 99.85% pure alumina powders with a particle size 0.150μm and 35μm were used for ceramic/binder mixtures of rods, tubes, and tapes.

Carbon Black: The co-extrusion process was developed using carbon as the sacrificial material. Here, carbon black BP 120 (1.8 g/cm³) was used from Cabot Corporation.

Glass Material: Alkali borosilicate glass powder (7056) was used with alumina powder to decrease the sintering temperature. This was provided by Corning Inc. with a particle size of 25μm. A mixture of alumina and glass particles was batched with binders in a HAAKE rheometer. The softening point of glass material is 718°C, where the CTE (0-300°C) is 5.15x10⁻⁷/°C.

2.1.2 Binder Components

Binder formulations were studied based on four materials, where compositions are shown in Table 2.1. A backbone binder was used to maintain the green strength, and PEG was used as a water soluble binder. Two molecular weights of PEG were used: PEG6000 (Alfa Aesar) as a binder and PEG200 (J.T.
Figure 2.1: Schematic diagram for processing steps of ceramic components with optional embossing step

Figure 2.2: Front view of partially filled torque rheometer with counter rotating blades
Table 2.1: Compositions (vol%) of all mixtures.

<table>
<thead>
<tr>
<th>Mixture (PEBA:PEG)</th>
<th>Al$_2$O$_3$/(Carbon)</th>
<th>PEBA</th>
<th>PEG6000</th>
<th>PEG200/(HMO)</th>
<th>Barrel Temp.(°C)</th>
<th>Die Temp.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic Mix1 (1:0)</td>
<td>55.35</td>
<td>40.78</td>
<td>–</td>
<td>(3.88)</td>
<td>130</td>
<td>135</td>
</tr>
<tr>
<td>Ceramic Mix2 (2:1)</td>
<td>55.37</td>
<td>29.29</td>
<td>11.84</td>
<td>3.50</td>
<td>115</td>
<td>120</td>
</tr>
<tr>
<td>Ceramic Mix3 (1:1)</td>
<td>55.68</td>
<td>22.09</td>
<td>18.71</td>
<td>3.52</td>
<td>110</td>
<td>115</td>
</tr>
<tr>
<td>Ceramic Mix4 (1:2)</td>
<td>55.52</td>
<td>14.68</td>
<td>26.29</td>
<td>3.51</td>
<td>105</td>
<td>110</td>
</tr>
<tr>
<td>Carbon Core (1:1)</td>
<td>(50.52)</td>
<td>24.96</td>
<td>21.03</td>
<td>3.51</td>
<td>110</td>
<td>115</td>
</tr>
</tbody>
</table>

Baker) as a plasticizer. The melting point of PEG6000 is 65°C and the density is 1.21 g/cm$^3$. For the control mixture without soluble component, heavy mineral oil (HMO, Fisher Scientific) was used as a plasticizer. Feedstocks with binders at different amounts of PEG (Table 2.1) were investigated using PEBA (35-BA-40) in (Sec. 3.1). A total of four different ratios of thermoplastic polymer to PEG were batched where the PEG amount increased while PEBA was reduced; the 1:1 mixture by volume of thermoplastic binder to PEG showed satisfactory results.

The 1:1 ratio mixture has been chosen to observe the effect of backbone binder on the two-step debinding process; 35-BA-40 was replaced with four other thermoplastic binders (Table 2.2). A total of five different thermoplastic blends was used in this study, where three grades of PEBA (Lotryl, Arkema Inc.) and two grades of EVA (Sigma Aldrich) with different melt indices were considered. PEBA is a random co-polymer of ethylene and butyl acrylate and EVA contains vinyl acetate.

The 1:1 ratio mixture is further chosen for glass-ceramic mixtures. A total of five mixtures was formulated to study a low temperature sintering ceramic material for microfluidic chip fabrications. Mixture compositions are explained in Chapter 5.

2.2 Processing of Feedstocks

Figure 2.1 shows a diagram of processing steps, all of which are described in following sections. Embossing is marked with a dotted line, because it was used only when microfluidic devices were manufactured.

2.2.1 Feedstock Batching

All binder materials were batched with precursor powders in a HAAKE Rheocord 90 (Rheomix 600) torque rheometer at 30 rpm and 130°C. Torque rheometers are batch mixers widely used in polymer processing and it measures the torque on the mixing blades. The volume of the mixing chamber with
Table 2.2: Overview of feedstocks: selected properties of thermoplastic binders, batch compositions, and conditions for extrusion.

<table>
<thead>
<tr>
<th></th>
<th>PEBA (Lotryl)</th>
<th>EVA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermoplastic Binder:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grade</td>
<td>17-BA-07 35-BA-40 28-BA-175</td>
<td>12-EVA-08 25-EVA-19</td>
</tr>
<tr>
<td>MFI (g/10min)</td>
<td>6.5-8.0 35-45 150-200</td>
<td>8 19</td>
</tr>
<tr>
<td>MP (°C)</td>
<td>89 72 80</td>
<td>95 75</td>
</tr>
<tr>
<td>Acrylate/Acetate Content (wt.%)</td>
<td>16-19 32-37 26-30</td>
<td>12 25</td>
</tr>
<tr>
<td>Density (gm/cc)</td>
<td>0.933 0.933 0.933</td>
<td>0.933 0.941</td>
</tr>
<tr>
<td><strong>Batch Composition (vol.%):</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina</td>
<td>55.68 55.68 55.68</td>
<td>55.72 55.25</td>
</tr>
<tr>
<td>Thermoplastic Binder</td>
<td>22.09 22.09 22.09</td>
<td>22.03 22.69</td>
</tr>
<tr>
<td>PEG 6000</td>
<td>18.71 18.71 18.71</td>
<td>18.73 18.56</td>
</tr>
<tr>
<td>PEG 200</td>
<td>3.52 3.52 3.52</td>
<td>3.52 3.49</td>
</tr>
<tr>
<td><strong>Extrusion Conditions:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barrel Temperature (°C)</td>
<td>115 110 100</td>
<td>125 120</td>
</tr>
<tr>
<td>Die Temperature (°C)</td>
<td>120 115 105</td>
<td>130 125</td>
</tr>
<tr>
<td>Ram speed (mm/min)</td>
<td>7.62 7.62 7.62</td>
<td>2.54 2.54</td>
</tr>
</tbody>
</table>

roller blades was 69 cc and 70% of the volume was filled to create a mixture. Figure 2.2 shows a front view of the mixing chamber with a filling degree of 70%. For batching, half of the powder and half of PEG6000 were added simultaneously to the molten thermoplastic binder, while the powder loading was 55vol% to ensure densification [41]. The remaining powder and PEG6000 were added slowly and the viscosity was adjusted using PEG200 before kneading the mixture for 25 minutes. All batches were processed twice to ensure homogeneity of the batched mixtures. Table 2.1 and 2.2 list mixture compositions prepared for alumina rods/tubes in this study. For batching glass-ceramic mixtures, the same procedure was followed where glass and alumina powder were mixed gradually to the molten binder system.

2.2.2 Mixture Rheology

A good understanding of binder system rheology is important for co-extrusion. The main challenge of co-extrusion is the processing of dissimilar materials that maintain the geometric shape without axial and cross-sectional deformation after co-extrusion [4]. Defect-free products require a detailed rheological characterization of materials to be co-extruded. Differences in the flow properties of the materials being extruded can lead to the formation of instabilities.

To obtain rheological data during batch mixing, equilibrium torque values from the HAAKE Rheo-
Figure 2.3: Image showing the ram extruder with compression frame
cord were recorded at rotor speeds from 10rpm to 40rpm with steps of 10rpm at two different temperatures. Based on torque measurements, the rheology was quantified by obtaining fits for a power law of torque versus RPM data [41, 45], which takes the form

\[ M = CN^n \]  

(2.1)

Here, \( M \) is the measured torque and \( N \) is the roller speed. Based on measurement data, \( C \) and \( n \) are obtained from straight line fits on the plot of \( \log(M) \) versus \( \log(N) \) [41].

For co-extrusion, rheological properties of dissimilar blends need to be matched, where the approach by Ismael et al. was followed [4]. The model is based on the assumption that the shear stress \( \tau \) is proportional to \( M \), and the shear rate \( \gamma \) is proportional to \( N \), i.e.

\[ \tau = K_1 M \]  

(2.2)

\[ \gamma = K_2 N \]  

(2.3)

The parameters \( K_1 \) and \( K_2 \) are constants which depend on the dimensions of the rheometer [44]. The apparent viscosity is then assessed as

\[ \eta = \frac{\tau}{\gamma} = \frac{K_1 M}{K_2 N} \propto \frac{M}{N} \]  

(2.4)

This relationship illustrates that the apparent viscosity is directly proportional to \( M/N \) [4].

To further quantify the apparent shear rate from torque rheometer measurements, the dimensional constant in Equation 2.3 is approximated as \( K_2 = \pi r/30y \), where \( r \) is the roller diameter and \( y \) is the gap between roller and wall [4]. Thus, the apparent shear rate is expressed in terms of \( N \) as

\[ \gamma_A = \frac{2\pi rN}{60y} \]  

(2.5)

where specific dimensions of \( r = 18.2mm/y = 1.4mm \) and \( r = 11mm/y = 8.6mm \) are used to estimate maximum and minimum shear rates, respectively.

The primary importance of Equation 2.5 is that it allows for an estimation of an appropriate extru-
The apparent shear rate for extrusions is given by

\[ \gamma_a = \frac{4Av}{\pi R^3} \]  

(2.6)

where \( A \) and \( v \) are the ram area and speed, and \( R \) is the die radius [4]. It is noted that for single material extrusions, the only restriction for extrusion speeds is the occurrence of surface defects. In the case of co-extrusion of dissimilar materials, however, viscosities need to be matched, which poses much tighter limits on the selection of suitable extrusion speeds.

### 2.2.3 Extrusion

Extrusions were performed with a custom ram extruder constructed from a 30 KN ComTen Universal Tester (95TL5K), where a barrel of 133mm length and 19mm diameter was mounted in a compression frame (Fig. 2.3). Two band heaters were used in the barrel and in the die region to control the temperature during extrusion. The feedstock material at the upper part of the barrel was cooled with circulating chilled water to prevent plastic deformation due to the longer time at a high temperature. Three hyper-
Bolic shaped dies with 5.84mm, 7.34mm, and 10.16mm diameter were used, which resulted in a size reduction of 10.5:1, 6.7:1, and 3.5:1 respectively. Feedrods were pressed into cylinders prior to extrusion. Extrusions were carried out at ram speeds ranging from 7.62mm/min to 2.54mm/min depending on the mixture types, where temperatures are listed in Table 2.1 and Table 2.2.

### 2.2.4 Co-extrusion

For co-extrusion, ceramic mixtures were pressed in a cylindrical shape and a hole was drilled in the ceramic shell. Sacrificial carbon black/binder material was extruded through the 7.34mm die and inserted into drilled holes of cylindrical ceramic feedrods/ceramic shells (Fig. 2.4). Co-extrusions were carried out using the same process where the choice of ram speed varied with viscosities of dissimilar materials (described in Section 2.2.2). Figures 2.4A (right side) illustrates the successful ceramic feedrod (diameter of 19mm), which consists of ceramic/binder as a shell and carbon black/binder as a core. The co-extrusion process produces the small diameter rod (2.4B). The dimensions of the carbon cores reveal exact size reduction, i.e., the extruded carbon core (2.2mm) is 10.5 times smaller than the preform (7.2mm), which is the same ratio as feedrod diameter (19mm) to die diameter (5.84mm). Although some distortions were found in the shape of the carbon core, ceramic shell and carbon core maintained the reduction ratio and visual inspection did not reveal other defects.

### 2.2.5 Tape Extrusion

For tape extrusion, a rectangular extruder was mounted in the compression frame instead of the cylindrical barrel. The rectangular section was formed with four separate steel walls of 100mm length and 7.62mm width. This section is combined with two sliding plates acting as die to control the thickness of the extruded tape (Fig. 2.5). A rectangular piston of 7.4mm thickness and 48mm width was used to press feedrods toward the die section. Two cartridge and two strip heaters were used to heat the material during tape extrusion. It had flexibility to control tape thicknesses where the thickness can be adjusted continuously from 0mm (closed) to 7.6mm (fully open). The width of the tape was 50mm, which was fixed. Material was fed from the top while two sliding brass plates closed off the bottom part. Material was heated to the desired temperature and pressed by a piston with a speed of 25mm/min to create a feedrod. After pressing, it was allowed to cool to room temperature. For extrusion, the brass plates were slid to an open position to get the required thickness. The extruded tape was cut in a length according to
the fluidic chip length.

2.2.6 Embossing

For embossing, a conventional hydraulic press (Carver Hot Press, model-3851-0, Carver, Inc) was used. The temperature of heated platens were controlled (Fig. 2.6). The bottom platen was movable, and the top one was fixed. The mold pattern with microchannels was placed on the bottom platen and the temperature control system was set to the desired temperature. Demolding agent (Endurance Mold Release, Stoner, A353) was used on the mold to improve the ease of demolding. Once the temperature reached the desired point, flat tapes were aligned with the mold and an aluminum plate was placed on top as a backing plate. Precision steel spacers were used between the mold and the aluminum plate to control the thickness of the sample. The platens are brought together manually and pressed at 50psi. The platens are released immediately and samples were taken out and cooled at room temperature. Demolding was done at room temperature.
Figure 2.6: A schematic diagram showing the arrangement for embossing in a hot press machine

In the initial study, ceramic rods with a diameter of 10.16mm were pre-heated in a convection oven for approximately 10 minutes to soften the material until it was able to be pressed. This pre-pressing was done at 120°C by placing the rod between two platens and then cooled at room temperature to get a flat substrate. However, a longitudinal crack was found at the middle of sample, which is attributed to applied stress.

In subsequent work, ceramic material was extruded in tape extruder to obtain well defined rectangular substrates. For glass-ceramic mixture, extruded rods were embossed directly without creating flat substrate. Glass-ceramic materials were joined together to form a wider sample. Though ceramic rods were pressed similar to glass-ceramic; it did not work (Section 5.1.3).

2.3 Binder Removal
The binder was removed in three steps for all types of ceramic objects to get defect free samples: i) solvent extraction (SE) to initiate interstitial pore space, ii) thermal debinding in N₂ (TD₉₂) to promote pyrolysis of organic binders, and iii) thermal debinding in air (TD₉) to remove carbon residues.

2.3.1 Solvent Extraction in Water
SE was performed by immersing the samples in a water bath in a controlled temperature environment. To investigate the effect of temperature and extraction time on PEG removal, tests were performed by changing the water temperature from room temperature to 45°C, and extraction times ranging from 1h to 6hs for PEBA samples and up to 10hs for EVA samples. After extraction, samples were dried at room temperature until constant weights were obtained. PEG weight loss was calculated as a percentage of the original PEG content. For each solvent extraction condition, five samples were obtained and the average
PEG loss was documented. Measurement uncertainties were calculated by a Student-t distribution. PEG loss data was also verified by TGA tests under a N\textsubscript{2} atmosphere with a ramping rate of 2.5°C/min up to 800°C. In order to verify that solvent extraction creates pore space, extracted Mix3 (1:1) samples were again immersed in water and the wet weight was recorded. Results for pore space volume calculated from PEG loss and water incorporation matched within 5%, where the small discrepancy is attributed to incomplete permeation and/or minor swelling of residual PEG.

### 2.3.2 Thermal Debinding

TD was performed in a tube furnace with a heating rate of 1.25°C/min up to 1000°C for all alumina extruded tubes and embossed samples. Although TGA result shows that all the binder was removed at 600°C, heating was continued to a higher temperature to initiate pre-sintering. In the case of glass-ceramic samples, TD was carried out at the same heating rate to 600°C to prevent premature liquid-phase sintering. Samples without extraction tests were tested in only air, and a combination of N\textsubscript{2} and air; cracks showed in both cases. To prevent the formation of cracks, TD was carried out in two stages with N\textsubscript{2} and air after extraction, respectively. Here, the inert N\textsubscript{2} atmosphere minimizes the rate of oxidation reactions, and subsequent heating in air removes remaining carbon from the sample.
2.4 Sintering

After binder removal, alumina samples were sintered using three cycles with a 1h hold at 1600°C in a high temperature furnace. For the glass-ceramic materials, sintering temperature was decreased. Depending on the glass amount, different sintering temperatures were achieved for glass-ceramic mixtures. The lowest sintering temperature was found at 800°C for 50:50 ratio of glass to ceramic mixtures.

2.5 Capping

For capping, borosilicate glass slides (cole-parmer) were used to cover embossed fluidic chips. For both ceramic and glass-ceramic samples, glass slides were bonded by a thermal process. After sintering, the glass top was put on the fluidic chip without any pressure and was heated to the glass softening point with 1h dwell time. An annealing cycle was required after the bonding cycle to avoid cracks due to residual stress.

2.6 Characterization Tests

2.6.1 TGA

A TA Instrument DSC Q500 was used for the thermogravimetric analysis (TGA) of ceramic samples. Tests were conducted in the presence of the N₂ atmosphere with a ramping rate of 2.5°C/min up to 800°C. All TGA test samples were subjected to a heat/cool cycles ramp from room temperature to 800°C and cooling to room temperature.

2.6.2 Optical Microscopy (OM) and Scanning Electron Microscopy (SEM)

Sample morphologies were studied for both green and sintered specimen. Optical micrographs (LEICA MZ75) were used to illustrate the shrinking core during SE and defects found after TD. A lumar microscope was used to analyze microfluidic channels for ceramic and glass-ceramic samples. ImageJ [91] software was used to measure the core radius in the optical images, where a measurement uncertainty of 20% was assumed. Details on the microstructure of green and sintered specimen were investigated using two scanning electron microscopes: (SEM) (FEITM, Quanta 3D FEG) and JEOL JSM-6610LV. For SEM imaging, samples were coated with platinum by the EMS 550X Sputter coater.
2.6.3 Profiles of Embossed Samples

The detailed metrology for depth profiles of the embossed sample was performed by an optical profilometer (Nanovea ST400, Micro Photonic Inc., Allentown, PA, USA). The flatness of tape substrate for fabricating microgrooved structures was also checked using this profilometer. Deviations of about $\pm 5$ microns were accepted for flatness of micropattern embossing. A measuroscope was used to measure the width of channels of embossed samples.
Chapter 3
Debinding and Sintering of Co-extruded Ceramic Components

This chapter describes the two-step debinding process introducing both solvent extraction (SE) and thermal debinding (TD) and sintering results for co-extruded ceramic tubes. Feasibility of this combined SE/TD debinding process for a binder system that is suitable for polymer co-extrusion is documented in Section 3.1 (published in a referred journal [92]). In Section 3.2 the choice of thermoplastic backbone binders is investigated (published in a referred journal [93]). A partially soluble binder system consisting of high molecular weight PEG6000 and low molecular weight PEG200 (Table 2.1 and 2.2) was used to avoid debinding defects. The overall debinding process and the effect of thermoplastic binders are reported here for the extrusion of solid ceramic rods and co-extrusion of tubes. Morphology tests on the both green bodies and sintered samples are presented.

3.1 Two-step Debinding Process

A two-step binder removal process is demonstrated here with a partially soluble PEG binder system. A thermoplastic backbone binder PEBA was batched with PEG at three different ratios and a conventional PEBA mixture without soluble components was used as a control. The effect of ratio between thermoplastic binder and PEG content on debinding process was studied. The combined SE/TD process was also investigated for varying solvent temperatures, extraction times and debinding atmospheres.

3.1.1 Debinding Defects Without Extraction

Traditionally, binder is removed by 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. In order to verify the requirement for a two-step debinding process, TD tests without prior SE were performed for all blends. In addition to tests with PEBA:PEG mixtures, a control mixture without PEG component (Mix1; PEBA:PEG=1:0) was subjected to TD to investigate the impact of PEG. Figure 3.1 shows results for the N\(_2\)+air and air only burnouts without extraction tests. The control mixture without PEG, Mix1 (1:0), was run in both air and a sequence of inert gas (N\(_2\)) and air. Although the inclusion of TD in N\(_2\) improved results, defects were found in both cases (Fig. 3.1a and 3.1b). Without N\(_2\), cracking is
Figure 3.1: Optical images showing the effect on macroscopic defects after TD without SE: a) Mix1 (1:0) – in air, b) Mix1 (1:0) – in N₂ and air, c) Mix2 (2:1) – in air, d) Mix2 (2:1) in N₂ and air.
attributed to excessively fast oxidation; in both cases, a lack of open pores initiated the formation of blisters [28]. Samples of Mix2 (2:1), which contain PEG but were not subjected to SE, also showed defects when run in air and a combination of both atmospheres (Fig. 3.1c and 3.1d), although defects manifested themselves in cracks rather than blisters. As an alternative to TD, SE was applied prior to TD with a soluble binder and can be removed to create a porous structure.

3.1.2 Binder Removal by SE

**SE Process:** Solvent extraction is a two-stage process consisting of dissolution and diffusion [11, 30]. Once 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 [51]. This partial removal of the binder created pore space and as the debinding time increased, the pore spaces were expanding to the inner region of the sample and formed a clear boundary between an outer shell where PEG has been removed and an inner core with undissolved PEG. A combination of SE and TD has been proven to be an efficient approach to eliminate defects [10, 17]. Pore space created during the initial SE step allowed pyrolysis gases to escape during subsequent TD, and thus lead to a reduction of cracks [30, 31].

As the extraction time increased, the radius of the undissolved core decreased, as shown in Figure 3.2. A comparison of extraction for Mix3 (1:1) and Mix2 (2:1) at 35°C showed a significantly faster core
removal for the sample with higher PEG content: for Mix3 (1:1), no visible core remained after 2h, while for Mix2 (2:1), a small core was still visible after 6h. The occurrence of a moving boundary is consistent with previous studies on solvent extraction [30, 34]. A schematic diagram for both core and outer shell is shown in Figure 3.3. During SE, when PEG comes into contact with water, it starts to swell. As the debinding continues, PEG molecules started to dissolve with time as well as the depth of water increases inside the samples from surface to center. Pore channels are expanding to the inner side of the sample as the boundary is moving to the center (Fig. 3.3) and an unextracted core shrinks with extraction time until it vanishes (Fig. 3.2).

**Effect of Time and Temperature on PEG Extraction:** In a preliminary test, the effect of extraction time was studied for solid ceramic rods for all 3 mixtures with PEG. For SE, 25.4 mm long extruded rod samples were immersed in water at room temperature (RT), 35°C and 45°C, for durations ranging from 1 to 6hs. As expected, the percentages of PEG removal increased with time for all mixtures, where Mix3 (1:1) showed 80wt.% of PEG removal after 6h extraction, which is comparable to PEG removal reported
Figure 3.4: PEG loss of ceramic samples as a function of extraction time: a) comparison of different mixtures at a solvent temperature of 45°C, and b) effect of solvent temperature on SE for Mix2 (2:1).
in the literature [11, 17, 94]. Likewise, results show higher PEG removal rates for mixtures with higher PEG content at comparable extraction times, which was due to the effect of increased porosity formed by the larger amount of PEG in the mixture. Tests with Mix4 (1:2) formed an exception, where swelling was observed after two hours of extraction, and material strength was insufficient for further processing after PEG removal. Compared to all other mixtures, Mix4 (1:2) has the smallest amount of thermoplastic backbone binder; swelling stress increased the volume of samples, which is a documented process for crack formation [17]. The extraction test was repeated for co-extruded rods with Mix2 (2:1) and Mix3 (1:1). Figure 3.4a shows the effect of solvent extraction time on the PEG removal at 45°C for solid rods and co-extruded rods. It showed PEG removal percentages were analogous to the PEG removal from solid rods: after 6h, solvent extraction removed ~70% of PEG in Mix2 (2:1) and ~80% of PEG in Mix3 (1:1). The amount of lost PEG was verified by TGA tests for samples from Mix3 (1:1) shown in Figure 3.5.

Figure 3.4b illustrates the effect of temperature on PEG lost for Mix2 (2:1) at three temperatures. It is observed that, as the temperature increased from room temperature to 45°C, PEG removal percentages were increased. At higher temperature, PEG dissolving was promoted due to an increase of the solubility of PEG in water [10, 17], which enhanced PEG removal.
Figure 3.6 shows measurements of the unextracted core radius for Mix2 (2:1) as a function of extraction time and water temperature. Specimen subjected to extraction at room temperature and 35°C had cores up to 6 hours and at 45°C up to 4 hours. Samples maintained the shape during extraction and showed good structural integrity after drying. A comparison of results for weight loss and core radius revealed that the core vanishes when a sample lost approximately 60 wt.% of PEG. In analogy to results for core shrinkage, the rate of PEG removal was observed to increase as the temperature was raised from room temperature to 45°C.

**Pore Structure Development During Solvent Extraction:** Figure 3.7 shows cross-sectional SEM images for Mix2 (2:1) after 4h SE. For the core region, Figure 3.7a demonstrates that there was no pore or void space as undissolved PEG was still present in this region. At the interface (Fig. 3.7b), small pores between strands of polymer binder are apparent. The more PEG was extracted at the outer shell area, the more void spaces or pores were formed (Fig. 3.7c). During thermal debinding, these pores allowed the pyrolysis products to escape from the sample.

The microstructure of the alumina-PEBA-PEG blend plays a major role in the success of solvent extraction. Tests with an unfilled PEBA/PEG mixture revealed that PEBA and PEG do not mix and remain phase separated. While filler material enforces dispersion of the phases throughout the mixture, phase separation of PEBA and PEG will persist at the microscale, which is expected to form a three-phase mix-
ture. According to percolation theory [95], contiguous PEG regions exist as long as a sufficient volume percentage of PEG is present. After solvent extraction, a PEBA-alumina network with contiguous pore space remains, which is corroborated by the SEM images shown in Figures 3.7b and 3.7c.

### 3.1.3 Thermal Debinding

**TGA Test:** The weight change during TD was evaluated using TGA (Fig. 3.5). Mix3 (1:1) decomposed in three steps where the first loss occurred in the temperature range of 80°C–250°C due to the elimination of crystallization water. The second step of weight loss combined the decomposition of PEG [53, 49] in the range of 300°C – 410°C and PEBA in the range of 250°C – 520°C. A sharp weight drop around 300°C was attributed to rapid volatization of PEG 200, whereas PEG with higher molecular weights decomposed at higher temperatures over a broader range of temperatures [96]. In the third step, weight loss occurred due to carbon loss in air. In Figure 3.5, sample ‘a’ (before SE), showed a total weight loss of about 17.67wt.%, which was close to the total binder weight percentage of 17.45% in Mix3 (1:1). At the beginning (150°C-350°C), sample ‘c’ (6h SE) shows a faster weight loss than sample ‘b’ (2h SE), which was attributed to a larger amount of open pores available for outgassing. In theory, PEG is removed by SE from sample ‘c’. Minor discrepancies between theoretical and actual weight loss in the extracted sample were attributed to small amounts of residual PEG: even if the core was removed (Fig. 3.6), small amounts of PEG remain within the samples (Fig. 3.4).

**Effect of PEG on Thermal Debinding:** Several debinding protocols were investigated for the mixtures as listed in Table 3.1, where the results without SE is shown in Section 3.1.1. The impact of solvent extraction on defects was evaluated for samples with 2, 4 and 6hs of SE at 45 °C. In all cases, samples had initial pores before TD was run in N₂ followed by air; however after 2h SE, cracks were still found.

![Figure 3.7: SEM images of cross-sections formed by razor blade cuts after 4h solvent extraction at 35°C for Mix2 (2:1) samples: a) core, b) interface, and c) shell.](image-url)
Table 3.1: Overview of debinding protocols showing the impact of extraction time and debinding atmosphere.

<table>
<thead>
<tr>
<th>Mixture (PEBA:PEG)</th>
<th>SE</th>
<th>TD1</th>
<th>TD2</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix1 (1:0)</td>
<td>–</td>
<td>–</td>
<td>Air</td>
<td>blisters, cracks</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>N₂</td>
<td>Air</td>
<td>blisters</td>
</tr>
<tr>
<td>Mix2 (2:1)</td>
<td>–</td>
<td>–</td>
<td>Air</td>
<td>cracks</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>N₂</td>
<td>Air</td>
<td>cracks</td>
</tr>
<tr>
<td></td>
<td>2h</td>
<td>N₂</td>
<td>Air</td>
<td>cracks</td>
</tr>
<tr>
<td></td>
<td>4h</td>
<td>N₂</td>
<td>Air</td>
<td>no defects</td>
</tr>
<tr>
<td></td>
<td>6h</td>
<td>N₂</td>
<td>Air</td>
<td>no defects</td>
</tr>
<tr>
<td>Mix3 (1:1)</td>
<td>2h</td>
<td>N₂</td>
<td>Air</td>
<td>no defects</td>
</tr>
<tr>
<td></td>
<td>4h</td>
<td>N₂</td>
<td>Air</td>
<td>no defects</td>
</tr>
<tr>
<td></td>
<td>6h</td>
<td>N₂</td>
<td>Air</td>
<td>no defects</td>
</tr>
<tr>
<td></td>
<td>6h</td>
<td>–</td>
<td>Air</td>
<td>cracks</td>
</tr>
</tbody>
</table>

Figure 3.8: Optical images after TD in N₂ and air showing the effect of SE on macroscopic defects: a) Mix2 (2:1) after 2h SE, b) Mix2 (2:1) after 4h SE, c) Mix2 (2:1) after 6h.

as illustrated in Figure 3.8a, as an unextracted core was only present for the 2h sample (Fig. 3.6). As either of the 4 and 6hs SE sample of Mix2 (2:1) showed no defects (Fig. 3.8b and c), the initiation of cracks in the 2h sample was attributed to the presence of an unextracted core. Tests were repeated for Mix3 (1:1) samples, which have a larger PEG content, and thus show increased PEG loss during SE. After SE, none of the 2, 4, and 6hs samples had an unextracted core; after TD in N₂ and air, samples showed no macroscopic defects or cracks. A final test for Mix3 (1:1) with 6h of SE but no intermediate burnout in N₂ resulted in a cracked sample.

3.1.4 Sintered Sample

The final sintered sample and the green sample of Mix3 are shown in Figure 3.9. It is observed that the sintered sample was reduced uniformly from the original green sample and fully sintered with a central hole (Fig. 3.9b). Detailed images show neither macroscopic nor microscopic defects. In order
to investigate microscopic defects, SEM images were obtained at the center of sintered solid samples of Mix3 (1:1). Figure 3.10a shows that microscopic cracks were present in the sample without SE, which is consistent with macroscopic cracks observed after TD. Although it did not show any macroscopic cracks after TD, Figure 3.10b reveals microscopic defects at the center of a sintered 2h extracted sample. Again, defects are attributed to insufficient initial pore space at the sample core due to insufficient PEG removal by SE. After 4h SE, enough pores were formed throughout the sample which resulted in a defect-free sintered specimen (Fig. 3.10c).

3.2 Thermoplastic Binders and Feedstock Characteristics

In this section, it is described how the binder choice affects the manufacturing process of sintered alumina rods. The combined SE/TD debinding process for polymer co-extrusion was applied to multiple ceramic-filled PEBA and EVA blends. In previous Section 3.1, 1:1 mixture showed the best result, different grades of PEBA and EVA materials have been chosen to study the binder removal process using a 1:1
Figure 3.11: Assessment of rheological properties for all ceramic-filled polymer blends measured on torque rheometer at different temperatures.
thermoplastic polymer:PEG ratio. Different binder interactions with ceramic powders and microstructures of sintered specimen were also investigated. In addition, it is explained how the PEG addition affects the co-extrusion process for a simple co-annular structure.

3.2.1 Mixing Behavior of Feedstocks

Figure 3.11 shows logarithmic plots of steady torque versus rotor speed as measured in the torque rheometer at 120°C and 125°C for the five blends considered in this study (Table 2.2). The torque decreased for all binder systems as the temperature increased, which corresponds to a decrease in melt viscosity as the mobility of polymer molecules is increased. Results reflected the expected trends with higher torque values for blends with lower melt flow index of the thermoplastic binder, which indicates a higher molecular weight. Higher molecular weights involve greater chain entanglements, which results in an increase of the melt viscosity [43].

In all cases, the blends were found to exhibit shear thinning behavior (pseudoplasticity) with \( n<1 \). Shear thinning was more pronounced for PEBA than for EVA samples, and increased with temperature.

Despite having nominally similar melt flow indices, torque values for 12-EVA-08 are higher than for 17-BA-07. Also, the EVA with the largest melt flow index (25-EVA-19) exhibits larger torques than the PEBA with the smallest melt flow index (17-BA-07). These results suggest that interactions between binder components and ceramic particles differ for EVA and PEBA samples. In order to test this hypothesis, PEBA-PEG and EVA-PEG blends were batched without ceramic filler. From visual observations it evident that PEBA and PEG do not mix, i.e. phases remain separated (described in
Section 3.1.2). Phase separation for tests with EVA blends was found to be less pronounced, and partial mixing was observed. This result is consistent with literature, where a fine dispersion of PEG within an EVA network was reported [97]. Based on this evidence, differences between rheological properties are attributed to differences in compatibility of PEG and the thermoplastic binder.

For extrusion tests, appropriate barrel and die temperatures were adjusted for each individual blend (Table 2.2). In general, higher temperatures are used for blends with higher viscosities, as the viscosity of the blend decreases with temperature, thus decreasing shear stress imparted on the extrudate. Appropriate extrusion temperature and ram speeds eliminate surface defects, which are illustrated in Figure 3.12. Results are shown for the blend with the highest viscosity (12-EVA-08), where periodic cracks (melt fractures) and loss of surface gloss (sharkskin [98]) were found for all tests at ram speeds larger than 2.54 mm/min. Loss of surface gloss was also observed for 17-BA-07 while extruding at 110°C and 7.62 mm/min; in this case, a temperature increase removed the defect. For EVA blends, temperatures were limited by the potential onset of binder decomposition, and the ram speed had to be decreased instead. It is noted that EVA blends exhibit less shear thinning as expressed by larger n values (Fig. 3.11). This is consistent with EVA being found to be more prone to surface defects, as the shear stresses at the surface are higher than for PEBA.

3.2.2 Effect of Binders on Two-step Debinding Process

SE on Different Thermoplastics Binders: With the exception of 28-BA-175 samples, all specimen maintained their shape during extraction after drying. PEBA samples with the lowest molecular weight (28-BA-175) showed cracks that are attributed to excessive swelling stress [17]; in the following, only the four blends that performed well during extraction were considered. Figure 3.13b shows the percentage of PEG extracted as a function extraction time. PEBA samples showed 80 wt.% of PEG removal after 6h, whereas EVA samples showed the same PEG removal after 10h. Faster removal of PEG from PEBA blends than from EVA blends is attributed to differences in the compatibility between PEG and thermoplastic binders, as previously discussed in Section 3.2.1. Due to this better dispersion and compatibility of PEG within EVA, the rate of PEG leaching from the EVA-PEG network was decreased, resulting in slower extraction.

The size evolution of the unextracted core is shown in Figure 3.14 for two representative PEBA and
Figure 3.13: Effect of extraction time on the weight loss of alumina rods with different binder system extracted in water at 45°C.
EVA blends. The slower rate of extraction for EVA is further illustrated in Figure 3.13a: the unextracted core region vanished after 2h extraction for PEBA samples, while it was 5h for EVA samples. However, in all cases a comparison of results for weight loss and core radius reveal that the core vanished when samples lost approximately 60wt.% of the original PEG content.

None of the EVA and PEBA samples showed evidence of external cracks after 2, 4, 6, 8 and 10hs of SE. Internal pore space created by SE allowed pyrolysis products to escape from the sample during TD. A complete extraction of the solid core was, however, necessary to avoid the formation of internal macroscopic defects or cracks. Consistent with previous results from PEBA in Section 3.1 [92], Figure 3.16 illustrates that the requirement of complete core removal held for EVA samples: after 4h extraction (Fig. 3.16a), about 1/3 of the outer diameter remained unextracted while about 50wt.% of the original PEG was extracted; the large internal crack is attributed to failure during TD. After 6h SE and 60wt.% of PEG loss, the unextracted core vanished, creating sufficient pore space throughout the sample and a defect free sintered specimen (Fig. 3.16b).

**TD for Different Binder Systems:** In order to test the difference between EVA and PEBA burn-out, samples were tested without SE. Comparing EVA and PEBA samples, it is observed that the defects in EVA samples are more pronounced, which is consistent with decreased stability at pyrolysis conditions [26]. TD in air only (Fig. 3.1) showed poor results, where warping of the samples was discernible. In all cases, samples displayed longitudinal and transverse cracking defects. Cracks are shown by blue arrows...
Figure 3.15: Optical images showing defects without extraction for samples from a) 17-BA-07, b) 35-BA-40, c) 12-EVA-08, and d) 25-EVA-19 in \( \text{N}_2 \) and air atm. (only air test results showed in the lower left corner for each of the samples)

In Figure 3.15. After extraction the 4h PEBA and 6h EVA samples showed no cracks as those had no unextracted PEG core.

### 3.2.3 Assessment of Sintered Samples

Figure 3.17 shows SEM images of fracture surfaces of sintered alumina rods fabricated from 17-BA-07 and 12-EVA-08 blends. Both images are from the largest extraction time, i.e. a 6h extracted 17-BA-07 sample and a 10h extracted 12-EVA-08 sample. It is clearly evident that samples exhibit good densification, and that both blends show comparable microstructures. Likewise, additional comparisons with samples fabricated from blends with different melt indices have similar results. This outcome validates that the choice of EVA or PEBA as thermoplastic binder has no effect on the success of the two-step debinding protocol, i.e. the tested binder systems yield the desired outcome with no discernible defects in sintered specimen.
Figure 3.16: SEM images of 12-EVA-08 samples after sintering: a) crack visible in 4h SE sample, b) no discernible debinding defect present in 6h sample.

Figure 3.17: SEM micrographs of transverse fracture surfaces of alumina rods sintered at 1600°C, a) 17-BA-07 blend, b) 12-EVA-08 blend.
Table 3.2: Parameters calculated for co-extrusion tests.

<table>
<thead>
<tr>
<th>Thermoplastic Blend</th>
<th>12-EVA-08</th>
<th>17-BA-07</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torque rheometer:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPM (1/min)</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>Shear rate range (1/s)</td>
<td>4.02-40.8</td>
<td>2.68-27.2</td>
</tr>
<tr>
<td>Viscosity ratio range (polymer/CB)</td>
<td>1.21-2.90</td>
<td>1.21-0.8</td>
</tr>
<tr>
<td>Co-extrusion:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity at apparent shear rate</td>
<td>1.12</td>
<td>0.99</td>
</tr>
<tr>
<td>Ram velocity (mm/min)</td>
<td>2.12</td>
<td>1.45</td>
</tr>
</tbody>
</table>

3.2.4 Co-extrusion of 12-EVA-08 and 17-BA-07 Blends

In order to assess the impact of PEG addition on the performance of co-extrusion of the resulting blends, tests were conducted for the fabrication of simple annular structures. Specifically, materials with the highest viscosities were selected for both EVA and PEBA as a base, i.e. 12-EVA-08 and 17-BA-07 (Table 2.2). In each case, the base material was used for the shell, whereas carbon black was substituted for alumina for the core. After co-extrusion, debinding and sintering, this process created tubular structures. As successful fabrication has already been demonstrated in Section 3.1, only the co-extrusion performance was evaluated here.

For co-extrusion, it is critical to match the viscosities of materials, as documented in available literature, e.g. [4]. In the following, the ratio $M/N$ is used as a metric for the apparent viscosity, as illustrated in Eq. 2.4. It is noted that geometric parameters $K_1$ and $K_2$ are functions of rheometer dimensions and thus are independent of the material. Figure 3.18 shows progressions of the apparent viscosity ratio $M/N$ as a function of RPM. Here, the target is to achieve the same M/N ratio for both materials to be extruded at their respective extrusion temperature. For PEBA, it showed matched apparent viscosity $M/N$ at 20 rpm; while it was 30 rpm for EVA blends. Based on the match, proper ram speeds for co-extrusion were obtained from Eqs. 2.5/2.6; results are summarized in Table 3.2.

To analyze the co-extrusion quality, ratios of carbon core area to the total tube area were evaluated experimentally and compared to their theoretical value. Results for multiple cross-sections along the extruded samples are shown in Figure 3.19. After an initial transient, EVA maintained the theoretical diameter where the extruded carbon core (2.2 mm) was 10.5 times smaller than the preform (7.2 mm). For PEBA, however, results show pronounced oscillations that correspond to instabilities that occur
Figure 3.18: Torque plots for thermoplastic blends loaded with alumina and carbon black as a function of RPM (squares mark conditions with matched viscosity).
Figure 3.19: Ratio of co-extruded carbon core area to total tube area as a function of co-extrudate volume (assuming 10% measurement error).

Figure 3.20: Optical images for co-extrudate of 12-EVA-08 (a, b, and c) and 17-BA-07 (d, e, and f).
despite carefully matched rheological properties of the blends. Figure 3.20 presents optical images for 12-EVA-08 and 17-BA-07 for three different zones (co-extrudate volume 3000mm$^3$, 7000mm$^3$, and 8800mm$^3$) where PEBA-PEG samples show more instability relative to EVA-PEG, indicating inferior quality for co-extrusion. The improved performance of co-extrusion of EVA-PEG blends is explained by a combination of higher viscosity and less pronounced shear thinning, where differences are attributed to a reduced compatibility between PEG and PEBA compared to PEG and EVA.

3.3 Summary

In Section 3.1 a two-step binder removal process involving both SE and TD is documented to eliminate debinding defects, where traditionally, binder is removed by thermal debinding (TD) in ceramic extrusion, which originates cracks or blisters. 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 80wt.% of the original PEG content after 6h extraction; after subsequent thermal debinding, rods and tubes sintered successfully without defects, demonstrating the viability of the process.

Section 3.2 investigated the choice of thermoplastic binders in a two-step debinding process. In total, five batches using alumina powder and a binder system with a 1:1 ratio of thermoplastic binder and PEG as water soluble binder were tested. Three grades of polyethylene butyl acrylate (PEBA) and two grades of polyethylene vinyl acetate (EVA) with different melt flow indices were investigated. In all cases, extraction tests resulted in 80wt.% removal of the original PEG content. However, PEBA samples showed a significantly faster PEG removal compared to EVA samples, which is attributed to a better dispersion of PEG within EVA. Tests with 4h extracted PEBA and 6h extracted EVA samples resulted in 60wt.% removal of PEG and a defect-free specimen after TD and sintering. Also, microstructures of sintered PEBA and EVA samples are comparable, which confirms that the choice of thermoplastic binders has no effect on the two-step debinding process. EVA-PEG feedstock showed higher stability in co-extrusion tests due to improved melt rheology and illustrate that EVA is better in co-extrusion.
Chapter 4
Embossed Microfluidic Devices

The purpose of this study is to investigate the feasibility of producing a new 3D rock based microfluidic chip by using sandstone. Sandstone is a sedimentary rock composed mainly of sand-sized minerals or rock grains. Till now, there is very limited research conducted on the rock based structures. Chenming et al. studied a mixture of “Pisha sandstone” with an activator solution to study the mechanical strength, where the mixture was pressed to specimens with a size of $d \times h = 50\text{mm} \times 50\text{mm}$ on a hydraulic testing machine [99]. Specimens were pushed out from the steel mold and cured in a oven at 80 °C for 24hs. This study is comparable with the ceramic processing of pressed samples [18, 61, 100]. These observations suggest that it is possible to utilize ceramic microfabrications to fabricate sandstone based microstructures.

As the fist step, this chapter documents a technique for fabricating micro channeled ceramic devices for microfluidic applications. Hot embossing was used to mold micro patterns on ceramic-polymer surfaces. Embossing offers a promising, cost-effective and fast method to generate microstructures on green substrates[11, 32, 33]. Embossing steps and characterization techniques are described as follows: mold and specimen preparation, embossing, demolding, sintering and capping. Characterization includes optical profiles for flatness, SEM and optical analysis of micro patterned samples.

A borosilicate glass was used as a cover for the microfluidic chip. It was sealed by thermal bonding heated at the glass softening point.

This embossing study is a collaboration with the microfluidics laboratory at Louisiana State University (LSU). Exploratory tests were done by polymer/ceramic mixtures from the extrusion work on ceramic fabrication and molds from the project of PMMA polymer fluidic chips (Microfluidics Laboratory, LSU).

4.1 Hot Embossing

In hot embossing, the substrate is heated to an elevated temperature and a mold is pressed into the material to form desired features [101]. Relatively low tooling cost, the ability to emboss on organic material, simple operation, and higher replication accuracy make it convenient over other methods like
chemical etching or silicon micromachining [15].

In this work, the developed firable green ceramic substrate, consisting of polymer binders and plasticizers (45vol.%), was used. Resembles natural rock structure, high temperature sustaining capability, availability and easy process ability present ceramic material well suited for the subsurface reservoir oil recovery. Ceramic-polymer materials flow slower compared to polymers during embossing. Process parameters for embossing were identified as temperature, pressure, holding time. Parameters were investigated to obtain appropriate combination for perfect embossing [33, 32].

After embossing of microfluidic patterns, it was followed by solvent extraction, thermal burn-out and sintering (Section 2.3 and 2.4). Binder materials constitute about 45vol.%, where burning out of the binder material resulted in a proportional shrinkage in the overall dimensions of microchanneled features. Shrinkage ratios of substrate length and width were 15-18% after sintering respectively. Hence, the shrinkage factor has to be considered in the initial design of this feature. Shrinkage-free in x-y directions ceramic tapes are, however, available from commercial vendors such as Heralock (HL2000 from Heraeus [32] and ZST (Sea Ceramic Technologies).
(a) Image of Brass mold B with full feature

(b) Left side: 3-D views of small footprint metrology locations for Mold B, and right side: dimensions for all sections (subscript letter shows color name)

<table>
<thead>
<tr>
<th>Width range (µm)</th>
<th>Layer</th>
<th>MI (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250-221</td>
<td>L_{L0}</td>
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<tr>
<td>221-193</td>
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<td>193-164</td>
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<tr>
<td>164-136</td>
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<td>136-107</td>
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<td>107-79</td>
<td>L_{L5}</td>
<td>30</td>
</tr>
<tr>
<td>79-50</td>
<td>L_{L6}</td>
<td>36</td>
</tr>
</tbody>
</table>

(b) Left side: 3-D views of small footprint metrology locations for Mold B, and right side: dimensions for all sections (subscript letter shows color name)

**Figure 4.2:** Brass mold B and a drawing shows different channel depth
Figure 4.3: Carver Hot Press- experimental set-up for embossing
4.2 Experimental Details

4.2.1 Mold

Mold plates, made of Brass metal (4.74 inch diameter), had been developed for embossing on PMMA polymer devices by D. Park and D. Nikitopolous (Microfluidics laboratory, LSU, supported by Advanced Energy Consortium) (Fig. 4.1 and 4.2a). Brass molds were used for microfabrications to study particle transport in artificial porous media. Micromilling was used for pattern fabrication with different sizes of diameter milling bits (KERN MMP-2522, KERN Micro Feinwerktechnik GmbH, Eschenlohe, Germany). There were multiple layers with different depth of channels in molds. Aspect ratio (channel depth/channel width) for mold A was a range of 3 to 1, while it was less than one for mold B.

In mold A, channels with 4 different widths from 50µm to 127µm and 4 different depths ranging from 50µm to 381µm were fabricated. A 3-D view of small footprint and metrology locations with color of mold B (different colors indicate different channel depths) is shown in Figure 4.2b. Total eight layers of different depths with a range of widths are listed in table (Fig. 4.2b). First, the highest depth channel was micromilled and then consequently grooved the lower depth channels.

4.2.2 Sample Preparation

The same procedure was followed here as described in Chapter 2 for the compositions of materials for feedstock preparation and extrusion. Flat substrates were prepared by two methods: (a) flattening of extruded rods and (b) tape extruding. Before the tape extruder was available, material was extruded as rods and then pressed in a hot press (Carver Hot Press, model-3851-0, Carver, Inc.) (Fig. 4.3) to create flat samples. Both PEBA and EVA materials were tested to emboss patterns. Comparing these two materials the 25-EVA-19 mixture was chosen for embossing due to better embossing quality. This is attributed to its higher viscosity and less pronounced shear thinning behavior (Chapter 3). Rods were pre-heated in a conventional oven at 100°C for 15mins before pressing. The platens were heated to the desired temperature, pre-heated rods were placed between the heated platen and a pressure of approximately 500psi was applied to flatten the rod. Pressure was released immediately and mold substrate assembly was removed from hot press and cooled at room temperature. In this method cracks were found in the middle of the sample, which was attributed to high stress.
Table 4.1: Physical properties of green ceramic tape

<table>
<thead>
<tr>
<th>Property</th>
<th>Ceramic-EVA mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic particle size, (µm)</td>
<td>.15</td>
</tr>
<tr>
<td>Ratio of ceramic powder to organic binder, (vol.%)</td>
<td>55:45</td>
</tr>
<tr>
<td>Fabrication method</td>
<td>Extrusion (at 120°C)</td>
</tr>
<tr>
<td>Green density, (gm/cc)</td>
<td>2.67</td>
</tr>
<tr>
<td>Theoretical Density</td>
<td>3.9</td>
</tr>
<tr>
<td>Thickness, (mm)</td>
<td>1-4</td>
</tr>
</tbody>
</table>

- **4.2.2.1 Tape Extrusion**

Feedstocks were extruded as flat tape and cut into the desired shape of chips. Tape extrusions were performed using a ram extruder mounted in a compression frame on a ComTen Universal Tester (95TL5K) (Chapter 2). Extrusions were carried out at temperatures ranging from 120°C to 130°C.

**Properties of Green Tape:** The total ceramic powder content of green material was 55 vol.%, and the remaining 45 vol.% consisted of binder polymers with a weight ratio of EVA/PEBA:PEGs:=1:1. The tape extruder allowed extruding different thicknesses of ceramic tapes. Extrudate can be cut to the desired green shape and embossed. The ultimate objective was to fabricate ceramic tapes in an efficient way as well as a cost-effective production. Green properties of ceramic tape are listed in Table 4.1. The green density was calculated from mass and volume of the tape at its green stage.

- **4.2.2.2 Embossing**

Replication of the microstructures were carried out by embossing. Embossing was performed at 120°C, while applied pressure was slowly increased up to 500psi by raising the bottom platen against the top platen. Figure 4.4 shows a sketch of temperature–pressure profile for embossing. Applied pressure was released immediately and the whole assembly of mold-substrate-backing plate was removed. The assembly was kept for 30mins to cool at room temperature. Demolding was done after the assembly was cooled completely to room temperature. The total embossing and demolding time was approximately 1h. After molding, two holes of 1mm were drilled at the inlet and outlet positions to provide entry and exit ports for fluid flow to channel structures (fluid transport mechanism will be performed in future by another group).

In order to check the quality of hot embossing, SEM analysis was performed on the fabricated microchanneled patterns on green ceramic-polymer substrates. Figure 4.5 shows the fabricated microfluidic
device with embossed features for EVA samples. These samples were embossed using mold A. Three positions are marked in green ceramic sample and SEM images of those positions are shown. No demolding defects were observed for green microgrooved samples.

4.3 Embossing Parameters

The embossing temperature is an important parameter for successful embossing. In this work, different embossing temperatures were used to study the appropriate temperature for embossing. A temperature of 110°C was insufficient to emboss the channel depth properly. Measuroscope and Profilometer measurements were performed to compare the embossed channel width and depth. Figure 4.6 shows optical images with embossing temperature variation in the range of 115°C to 125°C. At 130°C, ceramic-polymer
Figure 4.5: Green ceramic-polymer substrate with micro channel for mold A (Top image); SEM images of micro channel green samples- a) at position 1, b) at position 2, and c) at position 3

Figure 4.6: Optical images of microstructure at left corner of output side of a) mold B, and green sample of b) at 115°C, c) at 120°C, and d) 125°C
Figure 4.7: Optical profilometry on ceramic samples showing flatness at a) mold B, b) 115°C, and c) 120°C
mixture was very soft to emboss when applying pressure. Three temperatures - 115°C, 120°C, and 125°C were chosen to emboss. It was found that the temperature strongly influenced the resulting filling rate and the final quality of channels and cavities [76]. In Figure 4.6 it shows that a better molding accuracy was achieved at 115°C and 120°C.

Molded samples were evaluated in 12mm by 2mm area sections via optical profiler scanning at 10µm resolution, shown in Figure 4.7. Here, results illustrate a better flat surface at 120°C compared to the scan of mold insert. Though 5µm-8µm differences in depth existed for 120°C samples; however was much flatter than 115°C sample.

Several tests were performed at 120°C by changing the holding time at 500psi. Cracks were observed at the middle of embossed sample with any holding time. Finally crack free sample was found without any holding time, i.e. releasing the applied pressure immediately after embossing.
4.4 Demolding

After molding, the substrate needs to be separated from the mold. Demolding is one of the critical steps to fabricate microchanneled features by hot embossing. Demolding defects include broken or damaged features found in hot embossing, if the molding part was not separated perfectly. In hot embossing, a very commonly observed defect is bulge of one side of a feature (Fig. 4.8a) [16]. Other defects commonly found are broken mold features and leaving materials in mold features (Fig. 4.8b) [16].

In this study, it was difficult to separate ceramic-polymer material from the Brass mold during demolding. Figure 4.9 shows defects originating from demolding: circle marks indicate the warping or inappropriate filling due to slow material flow. It was also found that curvature shape of sample surface due to imperfect demolding (Fig. 4.10). To remove this problem, a mold release (Endurance Mold Release, Stoner, A353) was applied to the mold before heating in the hot press and samples were separated easily from the mold at room temperature. Figure 4.7 (at 120°C) shows a sample after demolding using the mold release spray, where no pulling was observed.
4.5 Characterization

4.5.1 Debinding Outcome

For the complete debinding protocol (Section 2.3), binder removal of the embossed chips involves two steps: SE and TD. SE is considered critical, as the dissolution of PEG in water creates a porous network which enabled the binder diffusion into the second debinding step [10, 92, 102]. In order to verify the requirement for a two-step debinding process, TD tests without prior SE were performed in previous work and samples displayed longitudinal and transverse cracking defects [93].

The channeled structures of the unextracted embossed sample and extracted sample are shown in Fig. 4.11 for ceramic-EVA mixture. During extraction, all samples maintained their shape and showed good structural integrity after drying at room temperature. No channel deformation was found due to PEG extraction from embossed chips.

After 3h SE, ceramic-polymer chips showed 63wt.% of PEG removal of the original PEG content for 2.5mm thickness. It showed earlier that 60wt.% PEG lost for 5mm thickness sample can achieve a defect free sample after sintering [93]. Therefore, all embossed samples were extracted for 3h at 45°C.

For TD, the same heating schedule as that developed for two-step debinding was followed [92]. It was reported from TGA tests that EVA totally decomposed at 550°C [48]. It confirmed that TD at 1000°C for 1h removed all EVA binder components. Binder component PEG200 rapidly decomposed [49, 53] at 300°C, whereas PEG with higher molecular weights (PEG6000) decomposed at higher temperatures over a broader range of temperatures (300 – 410°C) [92].
4.5.2 Sintering

The dimensional changes after sintering are clearly evident compared with the green sample (Fig. 4.12). The dotted line in green sample shows the reduced or shrinkage area of sintered chip in Figure 4.12. The total length of the green sample was around 50mm, while it was 40mm for the sintered sample. Although there was no visible dimensional changes after SE and thermal debinding, an approximate 17-21% shrinkage was found in x-y-z direction uniformly. Thus it can be considered during the design phase of the mold insert. No other defects or cracks were observed on the sintered component except shrinkage; good shape preservation of the channels confirmed from SEM analysis (Fig. 4.13).

The dimensions of selected small channels and blocks were measured to compare and analyze the shrinkage associated with the sintering process (Table 4.2). In Figure 4.14 six different points are marked and measured with imageJ software to calculate shrinkage.

Densities of the sintered ceramic samples were measured by geometrically and it was found that relative density of sintered sample was approximately 90%. In a previous study it showed that sintering
Figure 4.13: Comparison between SEM images of mold A feature (left images) and ceramic sample (right images) ("1" and "3" mark positions are shown in Figure 4.1 for mold A

Table 4.2: Dimensions of the Brass mold and sintered ceramic microfluidic sample sintered at 1600°C (W-width, H- height, and D- diameter)

<table>
<thead>
<tr>
<th>Positions/Dimensions</th>
<th>Brass mold B (μm)</th>
<th>Sintered ceramic sample (μm)</th>
<th>Shrinkage %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1W</td>
<td>12964.661</td>
<td>10148.148</td>
<td>21.724</td>
</tr>
<tr>
<td>1H</td>
<td>3131.977</td>
<td>2481.481</td>
<td>20.769</td>
</tr>
<tr>
<td>2D</td>
<td>2022.855</td>
<td>1629.63</td>
<td>19.439</td>
</tr>
<tr>
<td>3W</td>
<td>356.618</td>
<td>286.78</td>
<td>19.583</td>
</tr>
<tr>
<td>3H</td>
<td>389.71</td>
<td>328.302</td>
<td>15.757</td>
</tr>
<tr>
<td>4W</td>
<td>235.294</td>
<td>184.906</td>
<td>21.414</td>
</tr>
<tr>
<td>5W</td>
<td>286.765</td>
<td>241.509</td>
<td>15.781</td>
</tr>
<tr>
<td>5H</td>
<td>400.735</td>
<td>332.075</td>
<td>17.133</td>
</tr>
<tr>
<td>6W</td>
<td>183.824</td>
<td>150.943</td>
<td>17.887</td>
</tr>
</tbody>
</table>
Figure 4.14: Optical images- left images for mold B, and right images for sintered ceramic samples (numbers indicating different position)
at 1600°C for 1h achieved density of 90-93% of the theoretical density for this material [93].

4.5.3 Capping

Micropatterned ceramic chips need to be sealed to investigate fluid behavior in a leakage free device. The cover should be transparent; the transparency is an important factor to aid optical analysis. Ceramic-polymer material cannot be used as a cover due to the opacity. In this study a glass slide was attached to the ceramic chip as a cover by thermal bonding (Fig.4.15). For thermal bonding glass cover needs a fusion temperature between 650°C–800°C to initiate the softening of glass, but the surface tension forces of the molten glass help in maintaining the structure of the glass slide. Incomplete joining was reported by adhesive method (polypropylene glycol (PPG) and ethanol), where laminations of layered tapes were performed before sintering[15]. In case of bonding with adhesive or other materials, there is a chance to block the channel on microstructures. In this study, no pressure or adhesive was used, though some issues were found regarding the residual stresses of glass. Cracks were observed on cover slide after certain time of the bonding cycle. Cracks were removed by adding an annealing cycle after the bonding cycle finished.

The assembly was properly annealed at 550°C for 10mins and slowly cooled to room temperature (Fig. 4.16). The cooling rate was slow enough to get time to have the interior and exterior at the same temperature. The chip was completely cooled to room temperature before taking out from furnace.

Optical analysis was done to study the quality of capping. In Figure 4.15 (right image) darkar imprints revealed that the glass slide touching the ceramic chip. Though a good bond was obtained,
small portions were found where poor bonding was observed.

To check leakage, colored water was forced to flow through the channels, and no leakage of water was found.

4.6 Limitations

From the above discussions, it is clear that the ceramic-polymer substrate can be embossed with microchannels. Though embossing can be done successfully, there are some remaining issues described in the following sections.

4.6.1 Flatness

Initially it was tried to press circular rods, cracks were found at the middle of the sample which was attributed to stress. A tape extruder was built to get well defined flat tape instead of pressing rods. Using tape extrusion flatness was improved from 20\(\mu\)m to 5\(\mu\)m deviations.
Figure 4.17: Edge tearing observed in tape extrusion
4.6.2 Instability in Tape Extrusion

A brief description of tape extruder is given in Section 4.2.2.1. Edge cracking was observed for tape extrusion while for the same material circular extrusion was very smooth and was in perfect shape (Fig. 4.17). This is attributed to a result of lower extrusion ratio. Usually recommended extrusion ratios for ceramic range is between 10-100. However, the highest extrusion ratio is 6 in the constructed tape extrusion. Lower extrusion ratios can cause instability and edge cracking during extrusion [103] and a re-design is recommended.

4.6.3 Summary

This chapter presents ceramic-polymer materials as a viable candidate for microfluidic devices and describes a technique for ceramic microfabrication. Hot embossing was used to fabricate a micro chip for subsurface oil recovery analysis. Microstructures were formed on green substrates with high dependability, where flat tape was produced by tape extrusion. Lower viscosity of ceramic-EVA mixture at higher temperature was appropriate for extrusion and embossing process. A process temperature of 120°C with no holding time resulted the best embossing of microstructures. In comparison with embossed samples, dimensional changes after binder removal were not noticeable, although the dimensional changes after sintering was clearly evident. The embossed samples were sintered at 1600°C where 17-21% of dimensional shrinkage was observed in width and depth. Glass slides were attached successfully to cover ceramic chips by thermal bonding. Although cover was attached to the ceramic chip, additional tests are required for complete bonding where few points were poorly bonded. In addition, observed instability in tape extrusion need to be further investigated. Overall, the study describes new possibilities for microstructure fabrication on ceramic based substrate and established embossing process as a promising technique for fabrication.
Chapter 5
Fabrication and Characterization of Low Temperature Glass-Ceramic Components

This chapter demonstrates the fabrication of a low temperature sintered ceramic material and a microfluidic chip forming process as an example of application. Ceramic based microfluidic devices offer easy fabrication, high temperature stability, cost effectiveness, chemical inertness and 3D structuring capability. Borosilicate glass powder was added to ceramic powder to batch with polymer binder systems. A total of five different mixtures was fabricated and studied for embossing. Embossing was used to fabricate microstructures on glass-ceramic substrates. The quality of glass-ceramic compositions was evaluated by the density and the microstructure quality. After embossing, samples were processed by SE and TD. Finally, samples were sintered at a lower temperature compared to samples without glass. Optical and SEM images are included in this chapter to illustrate microstructures of channels.

5.1 Preparation of Green Glass-Ceramic Components

5.1.1 Batching of Powders and Binders

A borosilicate glass powder, Corning 7056, (Corning company) had been studied in this work. This glass contained SiO$_2$, Na$_2$O, Al$_2$O$_3$, B$_2$O$_3$, K$_2$O and Li$_2$O, where most of the content was SiO$_2$. The softening point of Corning 7056 was 718°C. The particle size of the glass powder was 25μm. Alumina powder (alpha phase, Inframat Advanced Materials) with two particle sizes of 0.15μm and 35μm were used in this study. The glass and alumina powders were mixed with binder systems in HAAKE rheometer in the same process described earlier (Section 2.2.1). The mixture was batched for 25 minutes twice to obtain a homogenous mixture. Due to satisfactory results all five mixtures were formulated with similar binder compositions of Mix 3 (1:1) where the ratio of thermoplastic binder to PEG was 1:1 (Section 3.1). For all compositions binder systems were same, while only glass contents were changing. Density of the glass-ceramic sample was calculated by the ratio rule, are listed in Table 5.1 with the composition of mixtures. Here, extruded circular rods are studied to check the sintering microstructure and density. Once a good density was found for any mixture, micropatterns were embossed.
Figure 5.1: Brass mold A made by micro milling for the fabrication of fluidic chip (recalled Fig. 4.1)

Table 5.1: Compositions of Glass-Ceramic Mixture (GCM)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Glass (wt.%)</th>
<th>Alumina (wt.%)</th>
<th>Density (g/cc)</th>
<th>Extrusion Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCM1</td>
<td>25</td>
<td>75</td>
<td>3.36</td>
<td>125</td>
</tr>
<tr>
<td>GCM2</td>
<td>33</td>
<td>66</td>
<td>3.19</td>
<td>120</td>
</tr>
<tr>
<td>GCM3</td>
<td>40</td>
<td>60</td>
<td>3.06</td>
<td>115</td>
</tr>
<tr>
<td>GCM4</td>
<td>50</td>
<td>50</td>
<td>2.91</td>
<td>115</td>
</tr>
<tr>
<td>GCM5</td>
<td>100</td>
<td>0</td>
<td>2.29</td>
<td>100</td>
</tr>
</tbody>
</table>
5.1.2 Extrusion of Round Rods

After batching with binder polymers, materials were extruded through the circular die (diameter 5.4mm). The overall process for the extrusion was described in Chapter 2. In comparison, extrusion temperatures for glass-ceramic samples depend on the different amount of glass content in it (temperatures are given in Table 5.1). After extrusion, samples were cut into small sizes to investigate the temperature effect on sintering and densification.

5.1.3 Embossing

The embossing mold A with three marked areas is shown in Figure 5.1. Micromilling with 25μm, 50μm and 100μm diameter was used for pattern fabrication in mold. Due to the coarse particle size of alumina (less fabrication accuracy), the mold B (used for ceramic) was not used for glass-ceramic material. From SEM analysis of alumina particles, it was found that most of the particle sizes were 50μm, which limited the use of mold B with feature sizes of 4μm-40μm.

For embossing, flat tape needs to be prepared with the glass-ceramic material. An instability was found in tape extruder during extrusion (Fig. 4.17); an alternative method was used to fabricate the flat tape. In the second method, two rods were directly placed on mold A and heated to a certain temperature (Fig. 5.2). It was kept for 10 minutes at the embossed temperature to soften the rod material to press. After pressing, it was held there approximately for 1 minute and released. The whole assembly was taken out and cooled to room temperature and demolded. To ease the demolding, a demolding agent was sprayed on mold A and was evaporated before pressing.

To investigate the quality of joint between two rods, sintered samples were cut in the lateral direction and investigated under an optical microscope. Figure 5.3 shows the cross-section of a sintered sample at 900°C. There was no separation found; while affirmed complete joining of two rods. In glass-ceramic mixtures glass material started to become softer at the embossing temperature and were spreading around the polymer and alumina. It created a glass-polymer network and interfered with the polymer chain-chain bonding providing more mobility to the polymer chain. Polymer expansions were increased in the presence of glass material in comparison to ceramic-binder mixtures [104, 105]. When two glass-ceramic rods were heated and pressed, materials can flow easily and attached to each other. In case of ceramic-binder, there was less polymer expansion for bonding during pressing and resulted a complete
Figure 5.2: Two glass-ceramic round rods placed on mold A for embossing directly
separation during embossing. All embossings experiments were performed by this process joining two glass-ceramic rods together.

Figure 5.4 shows features of the resulting embossed structure in the glass-ceramic mixture GCM3. Channels have aspect ratios in a range of 3 to 1 for positions “1” and “2” in Figure 5.1. Channels at “1” position were 50\(\mu\)m wide and 50\(\mu\)m deep. In Figure 5.4b, channels with minimum width was 127\(\mu\)m and minimum depth was 200\(\mu\)m. The shape of the channels and wall angle of the structures resulting from this embossing process were in exact shapes according to the mold structures. No material pulling was observed. It demonstrates that the micro feature patterned of the mold could be transferred to the green glass-ceramic material. A typical hot embossing cycle for this material was about 1h.

5.2 Solvent Extraction and Thermal Debinding

It is already known that for EVA samples 8 to 10h extraction time at 45\(^\circ\)C resulted defect free samples (Section 3.2). All glass-ceramic rods were extracted for 8h and embossed samples were extracted for 3h. PEG lost\% was calculated based on the original PEG content in green sample. Figure 5.5 shows the PEG lost\% for glass-ceramic (50:50) samples. It shows that PEG lost\% is increasing with increasing extraction time as seen before for ceramic samples. At 10h extraction about 95wt.\% of PEG was removed from samples, which created pores/void space in samples. These void spaces are required to release decomposition gases during thermal debinding [92]. For the embossed sample, 90wt.\% of PEG was removed during 3h extraction time. It was described in Chapter 3 that removal of 65wt.\% of PEG created a defect free sample. In this case, 3h extracted embossed samples should be defect free.

Figure 5.6 shows an extracted sample for 40:60 ratio mixture. Voids were formed when PEG was dis-
Figure 5.4: Embossing of microchannels of a fluidic chip on glass-ceramic substrates fabricated from a Brass mold, a) mold at area “1”, b) mold at area “2”, c) embossed green sample at “1”, and d) embossed green sample at “2” (as indicated in mold1)

Figure 5.5: PEG lost data for glass-ceramic sample (50:50) at 45°C along with extraction time
Figure 5.6: SEM images of extracted sample of glass-ceramic mixture after 8h extraction

Figure 5.7: Optical images for sample at “1” and “2” positions a) and b) after extraction, and c) and d) after thermal debinding
voids/pore spaces were found between polymer strands, as shown in Figure 5.6.

Due to a lower softening temperature of glass, the debinding schedule needed to be adjusted. Extracted samples were run at 600°C in N₂ and second run in air at 700°C to remove carbon from samples. An optical analysis was done to observe the effect of SE and TD. Glass-ceramic microfluidic chip channels after extraction and thermal burn-out are illustrated in Figure 5.7. It showed no swelling due to extraction; further no cracks were found in the sample after TD for 40:60 glass-ceramic samples.

5.3 Sintering

5.3.1 Shape Retention

Two positions (“2” and “3” in Fig. 4.1) of a sintered glass-ceramic microfluidic chip are shown in Figure 5.8. There was no damage of the walls or no other defects (cracking or chipping) were observed after sintering except dimensional shrinkage. Approximately 13-15% of shrinkage was found in z direction while 13-18% in x and y directions. Figure 5.9 shows an image of a sintered sample compared with
a green sample. At the same magnification, the sintered sample is visibly smaller than the green one.

It has been previously described that the densification of glass-ceramic samples can be shown by three-stage liquid-phase sintering[55] - particle rearrangement, dissolution and precipitation, and solid state sintering. In glass-ceramic sintering, glass forms a liquid and wets ceramic particles. Liquid is covering the solid surface and liquefaction of glass material dominates the viscous flow among particles. Making a liquid bridge between particles, friction between particles is reduced. The particles are rearranged easily under compressive capillary stress [55]. Hence the presence of liquid phase leads to enhance densification by increasing rearrangement of particles and matter transport through the liquid. If sufficient amount of liquid is present (in the range of 25-30vol %), movement of the particles in the liquid phase promotes a fully dense material [55].

5.3.2 Effects of Particle Size on Sintering

In initial tests glass material was batched with 0.15μm particle size of alumina and a poor density was found. In Figure 5.10, it shows relative density is increasing with temperature increasing. It was
Figure 5.10: A curve showing the effect of alumina particle size on density of glass-ceramic sample

Figure 5.11: Images of glass-ceramic (50:50 wt.%) rods after sintering at 1100°C showing elements of, a) Al, O, Si, K, b) only O, c) only Si, and d) only K (Al= aluminum, O= oxygen, Si= silicon, and K= potassium)
expected adding glass material to alumina should decrease the sintering temperature from 1600°C with a relative density above 90%; however at 1100°C, the highest relative density of 77% was found. This can be explained by the effect of particle size of alumina. Glass particle sizes (25 μm) were much larger than alumina particle sizes (.15 μm). In literature, it was found that smaller alumina with larger glass particles resulted poor density [57, 106]. Very fine alumina particles were hindering the glass liquid flow during sintering, which resulted in a poor density. It was reported that fine alumina particles (0.05 μm) dissolved in the glass liquids and increased the viscosity of glass which shifted the softening point of pure glass [106]. The dissolution of alumina particles slowed down the densification kinetics of glass-ceramic samples.

Figure 5.11 shows that glass particles are not redistributed homogeneously all over ceramic particles for 50:50 ratio with smaller alumina particle size. A number of pores were present even at 1100°C. It was necessary to maintain similarity between powder particle sizes.

To study this phenomenon, larger alumina particles (35 μm) were batched with glass and was processed up to sintering. At 800°C, density was found above 90% shown in Figure 5.10. From the SEM analysis of sintered sample, it shows that the new 50:50 glass-ceramic sample with larger alumina particle have a dense microstructure (Fig. 5.12b) compared to previous 50:50 sample. Samples of 50:50 ratio with larger particles sintered at 800°C, while with lower particle size showed highest density at 1100°C (Fig. 5.10).
5.3.3 Sintering Density

A better microstructure and density were obtained for larger alumina particle samples; four more mixtures were fabricated to study the effect of glass on the sintering process. Figure 5.13 shows the relationship between the relative density and the sintering temperature of glass-ceramic samples fired at different temperatures. The densification process for glass and ceramic is explained as liquid-phase sintering by considering that glass powders are uniformly dispersed in the glass phase matrix as the wettability between the glass and ceramic powder is good [107]. The relative density was calculated by taking the geometric dimensions. As expected, results show that increasing the amount of glass material increased the relative density at 800°C. High glass content samples showed good densification due to the higher content of liquid phase. Mixtures with 25:75 and 33:66 ratios showed higher density at higher sintering temperature, though the densities were poor. The sample with lower content of glass is difficult to densify and the maximum densification of 75% of the theoretical density was found at 1400°C. On the other hand, the relative density of the 50:50 and 40:60 ratios increased gradually up to 90% and 85% with increasing the sintering temperature. However there was also observed that a decreasing trend in density after a certain temperature. At higher temperature with lower content of ceramic, kinetics of viscous glass flow was very faster and redistribution of liquid flow was very prompt [106]. Glass softens rapidly
Table 5.2: Overview of the relative density of glass-ceramic samples with the amount of glass content

<table>
<thead>
<tr>
<th>Sintering Temperature (°C)</th>
<th>GCM1 (25:75)</th>
<th>GCM2 (33:66)</th>
<th>GCM3 (40:60)</th>
<th>GCM4 (50:50)</th>
</tr>
</thead>
<tbody>
<tr>
<td>720</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>83 ± 1.54</td>
</tr>
<tr>
<td>800</td>
<td>55 ± 0</td>
<td>62.66 ± 0</td>
<td>80.03 ± 1.09</td>
<td>92 ± 1.07</td>
</tr>
<tr>
<td>900</td>
<td>56.33</td>
<td>67</td>
<td>84 ± 1</td>
<td>88 ± 1</td>
</tr>
<tr>
<td>1000</td>
<td>57.25 ± 2.51</td>
<td>68.46 ± 1.53</td>
<td>82.33 ± 0.58</td>
<td>-</td>
</tr>
<tr>
<td>1100</td>
<td>57</td>
<td>70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1200</td>
<td>57.2 ± 0.84</td>
<td>70 ± 1.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1300</td>
<td>59</td>
<td>74</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1400</td>
<td>65</td>
<td>77</td>
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and dissolved gases were trapped, and resulted in pore formation in glass-ceramic structure [58, 57]. The samples with different glass contents have the different densification temperatures, i.e., 800 °C, 900 °C, 1300 °C and 1400 °C for 50:50, 40:60, 33:66 and 25:75 ratio glass:ceramic samples respectively.

5.3.4 Sintered Microstructure

The sintering mechanism of the system is described as liquid-phase sintering. SEM of fractured surfaces of samples are shown in Figure 5.14. Figure 5.14 shows SEM micrographs of glass-ceramic mixtures of 50:50, 40:60, 33:66, and 25:75 ratios at 800°C. It illustrates that with increasing glass content, pores were gradually decreased and increased density. A more complete densification was supported by the viscous flow of higher glass content in 50:50 ratio and fewer numbers of pores were recognized, which agrees with Figure 5.13.

For lower content of glass, Figure 5.15 shows microstructures at 1400°C. A 33:66 ratio mixture has lower voids/pores compared to a 25:75 ratio mixture.

5.4 Summary

Prospects of glass-ceramic material to produce complex 3D microstructure by embossing are described in this chapter. Microchannels with line width as small as 50 μm were embossed onto glass-ceramic green tapes. To create a flat tape for embossing, two round extruded rods were bonded directly during embossing. Images of the cross-section of sintered chip revealed complete joining of two rods. In optical and SEM analysis no deformations were found after extraction and thermal debinding.

The effects of alumina particle size and content on the densification of glass-ceramic were studied. Different sintering temperatures were found ranging from 800°C to 1400°C depending on the amount of glass present in mixture. The highest density was found for 50:50 ratio mixtures with larger particle size
Figure 5.14: SEM micrographs for fractured surfaces of glass-alumina samples with alumina content of (a) 75, (b) 66, (c) 60, and (d) 50 wt.% fired at 800°C for 60 min. (alumina particle size is 35 μm)

Figure 5.15: SEM micrographs for glass–ceramic samples sintered for 60 min at 1400°C for (a) 25:75 ratio, and (b) 33:66 ratio
at 800°C. At lower percentages of glass, poor densification was observed, while de-densification was found at higher temperature. A balance of these two phenomena is required to control the viscous flow of liquid to achieve a high densified glass-ceramic sample.

The achievements of this investigation and fabrication results demonstrated the feasibility of construction of microstructures on glass-ceramic materials and proved embossing as a viable method for fabricating low temperature glass-ceramic fluidic chip.
Chapter 6
Conclusions and Future Work

6.1 Conclusions

A complete processing route for co-extrusion and debinding of ceramic samples and fabrication of ceramic microstructures through embossing was investigated. The main challenge for the manufacturing process was to validate the feasibility of two-step debinding for extrusion (co-extrusion). To explore the potential applications of ceramic structures, microfluidic chips were fabricated and established hot embossing as a viable method for ceramic microfabrication. In addition, a low temperature sintered ceramic was fabricated as an alternative to commercial LTCC.

Two-step Debinding Process: Experiments involved ceramic-filled thermoplastic polymer blends, where alumina powder was mixed with polyethylene glycol (PEG) as soluble binder and either PEBA or EVA as the thermoplastic binder. PEG was added to the binder system to allow for solvent extraction. Binder removal of alumina rods or tubes, which were fabricated using a ram extruder, involved a combination of solvent extraction (SE) with thermal debinding (TD) in N₂ and air, after samples were sintered to full density. During solvent extraction, a moving boundary between an unextracted core and an extracted shell was clearly visible, where SEM images revealed interconnected void spaces in the extracted area. PEG removal increased with extraction time, and was accelerated by elevated temperature or increased PEG content within the mixture. Excessive amounts of PEG content led to a loss of green strength, where swelling was observed. A mixture with equal amounts of PEBA and PEG showed good PEG removal, with 80wt.% after 6h extraction at 45°C. Results demonstrate that debinding defects were eliminated by two measures: (a) contiguous interstitial pore space created by solvent extraction allowed for outgassing of products during thermal debinding, and (b) an initially inert atmosphere during thermal debinding promoted break-down of organic binders via pyrolysis rather than oxidation. Tests with PEBA:PEG mixtures showed that both measures are necessary for defect-free samples; residual carbon was removed with a second burnout step in air prior to sintering. The combined SE/TD debinding protocol with a soluble binder can be demonstrated as a successful alternative binder system for co-extrusion.
Effect of Thermoplastic Binder: After applying two-step debinding successfully, the follow-up study established that two-step debinding eliminates debinding defects irrespective of the choice of thermoplastic binders. It was also investigated that the binder choice affects the co-extrusion process. In total, five batches of binder system with a 1:1 ratio of thermoplastic binder and polyethylene glycol (PEG) with alumina were tested. Three grades of polyethylene butyl acrylate (PEBA) and two grades of polyethylene vinyl acetate (EVA) with different melt flow indices were investigated. While PEBA is relatively stable at pyrolysis conditions, EVA degrades rapidly and is thus more prone to cause debinding defects. SE was successful in all but one case, where high melt-flow index PEBA samples exhibited cracks that were attributed to swelling. In all cases, extraction tests resulted in 80wt.% removal of the original PEG content. No TD defects were observed as long as a core of undissolved PEG was fully removed by SE. On the other hand, all of the samples showed defects when SE was omitted, or when a residual undisolved PEG core was present. While defect-free densification was independent of the initial mixture, significant differences between blends were found in terms of rheology, debinding rate and co-extrusion. EVA-PEG blends showed higher viscosities and less pronounced shear thinning than PEBA-PEG blends. Furthermore, EVA-PEG blends show a significantly slower PEG removal rate than PEBA-PEG. In both cases, differences are explained by different compatibilities between PEG and the thermoplastic binder. EVA shows better compatibility with PEG than PEBA, and the slower removal rate and higher torque is attributed to a finer dispersion of PEG within the blend. Despite different removal rates during SE, both types of mixtures created a porous network that allowed for successful outgassing of pyrolysis gases during TD, which was completely removed during subsequent densification. The impact of PEG addition on the co-extrusion quality was assessed for two sample blends. Tests showed higher stability for co-extrusions of 12-EVA-08 compared to 17-BA-07 blends, which indicated improved melt rheology for EVA-PEG feedstock. Overall, results illustrate that two-step debinding allows for improved flexibility in the tuning of binder rheology for polymer co-extrusion: as long as a soluble component is present, solvent extraction eliminates thermal debinding defects irrespective of the thermoplastic binder.

Fabrication of Microfluidic Devices: Rods/tubes were fabricated and two-step debinding was validated as the first step. Successful manufacturing of ceramic structures (rods/tubes) benefits to build a ceramic microfluidic chip. A tape extruder was designed to obtain well-defined samples for ceramic tape
instead of compacted rods. Hot embossing was used to fabricate microstructures on ceramic substrates due to its simple operation and cost effectiveness. After sintering, 15%-20% of shrinkage was found in all directions, which can be designed during the initial planning time. Critical demolding issues were solved by using a demolding spray. To observe the effect of temperature, pressure and holding time for embossing, detailed metrology for microstructures and depths were performed on embossed samples. Good quality embossing was found at 120°C with an applied pressure of 50 psi for ceramic samples. To seal the chip, a glass top was placed on a sintered chip and a heat treatment cycle was performed at the softening temperature to bond the glass top with the substrate. Based on the observations there is a strong indication that micro embossing can be used as a viable method for fabricating ceramic-based microstructures.

In the second part of microfluidic fabrication a low temperature sintered ceramic material was fabricated by adding glass material as a sintering aid. Fabricated low temperature sintered ceramic has proved to be promising as a material for the development of microstructures for low temperature applications. Borosilicate glass was added at different ratios to investigate the sintering temperature and the microstructures. Hot embossing was used, which is established as a reliable method for fabricating microstructures in the first part. Lower particle sizes of alumina showed a detrimental effect on density of glass-ceramic; a good relative density of 90% was found for larger particle alumina for 50:50 ratios.

6.2 Suggested Future Work:

Extruder re-design: Edge cracking was observed for tape extrusion, described in Chapter 2. Ceramic tape extrusion was not perfect, as it showed instability during tape extrusion. It is required to re-design the material and die section to improve the extrudate quality.

Sealing: Although fabrication of microfluidic chips and sealing were successfully completed, small portions were found where poor bonding was observed. It needs to adjust the thermal bonding cycle to seal microfluidic chips.

Glass-ceramic mixture: Low temperature sintered ceramic was fabricated and micro patterns in the range of 25μm-300μm were embossed on it. Due to the coarse particle size of alumina (30μm-100μm), it was limited to emboss small features less than 25μm. It is suggested that to use similar size particles of glass and alumina.
Rock based microstructures: This study demonstrated the microfabrication on ceramic/glass-ceramic materials and sealing of fluidic chips. Based on this fabrication, real, rock based microfluidic device can be fabricated. The material properties and surface quality of rocks will be similar to the properties of actual oil subsurface reservoir areas. In this approach, sandstone rocks can be crushed into small particles as ceramic powders and batched with polymer binders. For microfabrication, the same process for ceramic fabrication will be followed.
References


Appendix
Microfluidic Chip for Fuel Quality Testing

From the idea of co-extrusion and ceramic embossing, microfluidic ceramic devices for fuel quality testing can be developed. Fluidic devices have potential applications in the area of alternative fuel research and internal combustion engines. To fabricate novel microfluidic fuel quality testing devices, few preliminary tests were done. Novelties of this work are the manufacturing process and component packaging with an integrated heater and diagnostic capabilities. Figure A.1 shows a schematic view of proposed fluidic chip to be developed and validated.

A.1 Materials and Manufacturing Approach

Ceramic will be the base material for main body and Nichrome (80%Ni20%Cr) and nickel will be the heating element and the connector, respectively. The base of the chip will be fabricated by co-extrusion to insert the heating element within the base material. After co-extrusion, a channeled structure will be embossed on ceramic base prior to debinding and sintering. In green stage, all electrical and fluidic connectors will be created. Due to high temperature applications quartz glass is to be used to seal the entire microfluidic device.

A.2 Fabrication

The base material was already developed in this study (Chapter 3) and demonstrated that microstructures can be embossed on ceramic-binder green samples (Chapter 4). Ceramic materials were batched with thermoplastic binder (ethylene vinyl acetate, EVA) in HAAKE rheometer. All binder components were removed by solvent extraction and thermal debinding. Sintering was done at 1600°C, while glass-ceramic-binder mixture was sintered at a lower temperature than 1600°C.

A.2.1 Batching of Nichrome and Nickel Mixtures

Nichrome mixtures were fabricated by 80wt.% of nickel and 20wt.% of chromium. Mixtures of both Nichrome and nickel were batched with the same binder system developed for ceramic materials (Chapter 2). It is important to match the sintering temperature of three mixtures (base material, heating element and connector) for co-sintering. Different amounts of glass were added to binder mixtures to equal the sintering temperature of three. Different sintering temperatures were found for glass-ceramic
samples based on the amount of glass contents (Chapter 5). However one mixture of nickel and one for Nichrome were fabricated for initial tests. Equal ratio of nickel and glass were used for nickel mixture; while 15wt.% of glass was used for Nichrome mixtures.

Matched viscosity of dissimilar materials at extrusion temperature is also critical for proper co-extrusion, described in Chapter 2. This needs to be done by rheology study for all three mixtures.

A.2.2 Extrusion

As preliminary tests, round rods were extruded for Nichrome and nickel mixtures separately to study the binder removal and sintering behavior. Co-extrusion of ceramic and Nichrome materials as flat tape was not done yet.
A.2.3 Binder Removal

Extruded rods were immersed in water to extract PEG for 8h. It was found that PEG losses for EVA binder systems in 8h extraction time were sufficient to obtain crack free samples. Approximately 85wt.% PEG was removed from Nichrome and nickel samples after 8h extraction at 45°C. Thermal debinding (TD) tests were performed in a reducing atmosphere to avoid oxide formations. TD1 was run in inert atmosphere up to 600°C at a ramping rate of 1.25°C/min. A reducing atmosphere was used for TD2 up to 700°C at the same ramping rate. The reducing atmosphere contained N2 and H2 in a ratio of 20:1. No deformation was found for nickel and Nichrome samples after binder removal.

A.2.4 Sintering

Nickel samples (with equal amount of glass materials) were sintered at 900°C. The relative density was found above 90%. This result has consistency with 50:50 ratios of glass-ceramic samples. However, Nichrome samples were not sintered even at 1100°C. SEM images of Nichrome mixtures sintered at 1100°C are shown in Figure A.2. Approximately 70% of relative density was obtained for Nichrome samples. There was a limitation to run at higher temperature in reducing atmosphere. No high temperature furnace was available with the facility of using reducing atmosphere. Hence sintering at higher temperature than 1100°C was not performed in this study. Sintering temperatures were not matched in these preliminary tests. To match the sintering temperature, glass percentages in nickel samples are required to decrease.

A.2.5 Conductivity Tests

To check the electrical conductivity of fabricated Nichrome and nickel samples, resistances were measured with a multimeter. Using resistance values and following equations, resistivity of Nichrome samples were calculated. Resistivity values were found in the range of 80x10^{-6} - 100x10^{-6} Ω-m.

\[ R_1 = \rho \times \frac{L_1}{A_1} \]

\[ R_2 = \rho \times \frac{L_2}{A_2} \]

Where \( \rho \) is the resistivity, \( R \) is the measured resistance, \( L \) is the length and \( A \) is the cross-sectional area of the sample.
For nickel samples, resistance values were found too high. The abundant amount of glass content formed nickel samples as non-conductive. It is required to decrease the glass amount for conductivity as well as to increase the sintering temperature.
Vita

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