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# Novel fabrication of injection-moulded ceramic parts with large section via partially water-debinding method

Wei Liu[a], Xianfeng Yang[b], Zhipeng Xie[a,*], Cui Jia[c], Linlin Wang[a]

[a] *State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China*
[b] *College of Physics and Electronic Science, Changsha University of Science & Technology, Changsha 410114, PR China*
[c] *The Palace Museum, Beijing 100009, PR China*

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## Abstract

In this work, we adopt a combination of low molecular weight PEG (L-PEG) and high molecular weight PEG (H-PEG) as water-soluble binder to fabricate injection-moulded ceramic parts with large section. The mechanism of the combination of PEGs removal was proposed for the first time. Defect-free near gear parts with large-sized-section (thickness – 16 mm) were successfully fabricated through water extraction (15 h) followed by rapid thermal pyrolysis (4.5 h). It solves the difficulty of fabricating injection-moulded ceramic parts with large section and our approach is energy saving and high-efficiency as compared with conventional thermal debinding. The results demonstrate that our approach of partially water-debinding followed by rapid thermal pyrolysis could solve the problems of conventional thermal debinding, providing an effective route for the production of injection moulded ceramic parts with large section.

*Keywords:* Injection moulding; Shaping; Defects; PEGs

## 1. Introduction

In recent years, ceramic injection moulding (CIM) has been recognised as a cost-effective process for the production of precise and complex-shaped ceramics with high performance in massive form.[1–4] This method usually comprises of four basic stages: mixing, moulding, debinding and sintering. Among the debinding methods, thermal debinding was the first process developed and is still widely used in the CIM industry because of its simplicity and the low investment of equipment.[4] However, the process is time-consuming because the debinding rate must be slow in order to avoid internal pressure buildup from decomposed binders, which causes cracking, blistering and exfoliation during debinding.[5–7] In addition, the successful manufacturing of injection-moulded ceramics by thermal debinding is only appropriate for components of relatively small cross-section (usually ∼3–5 mm).[8,9] For injection-moulded ceramic parts with large section, defects such as cracking, deformation and blistering still occur quite easily even if long thermal pyrolysis time is adopted. Because the length of mass transfer path for binder removal is proportional to the size of cross section for thermal debinding, it is difficult to fabricate defect-free ceramic parts with large section via thermal debinding.[9] Consequently, in practical production, if the cross section size of the ceramic parts is larger than ∼10 mm, almost all the manufactories adopt the moulding approaches such as dry pressing, slip casting and cold isostatic pressing. The organic binders used in the above approaches are much less than those used in injection moulding, so binder removal for such approaches is much easier than that for CIM. However, subsequent mechanical processing (grinding, lathing, cutting etc.) after pressing or sintering is necessary for such technologies because unlike CIM, they are not near net shaping technology, and this leads to high cost with brittle and rigid ceramic materials. In addition, as is known to us, the degree of continuous production of the above shaping technology is far away from that of CIM, which also increases the cost of the

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* Corresponding author. Tel.: +86 10 6279 9031; fax: +86 10 6277 1160.
*E-mail address:* xzp@mail.tsinghua.edu.cn (Z. Xie).

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production. Hence, it is necessary to seek a feasible debinding route to fabricate large-section-sized ceramic parts via injection moulding.

Partially water-debinding followed by rapid thermal pyrolysis appeared as a good alternative, for it presents both high efficiency and environmental acceptability.[10] For this approach, water-soluble binder is firstly removed while the interconnected pore channels are formed from exterior to interior, leaving the insoluble binders in the contact region and the pore channels could serve as escape paths for decomposed gas during subsequent thermal debinding for insoluble binders.[11] The binder system for water debinding mainly consists of water soluble components, which dissolve in water and insoluble backbone binder which keeps the strength of the green body in the whole debinding process.[12] Therefore, binder removal of water-based binder system is much easier than that of wax-based one since the pore channels originated from water-soluble binder could serve as escape paths for the following thermal pyrolysis as indicated above. Therefore, it may be feasible for water debinding to replace thermal debinding to fabricate ceramic parts with large section.

Most previous researches on water-debinding were focused on debinding dynamics, debinding mechanism, optimisation of binder system and microstructure evolution. Yang et al. proposed the solvent debinding mechanism and investigated microstructure evolution for alumina injection-moulded compacts with water soluble binders.[13] Tsai et al. investigated solvent debinding kinetics of alumina green bodies shaped by powder injection moulding.[14] Kim et al. investigated pore structure evolution and binder distribution during both solvent extraction and wicking.[15] Shivashankar and German introduced an effective length scale (the volume to surface area ratio) to understand the effect of the component's shape and dimensions on the critical heating rates for polymer burnout.[16] Yang et al. used the effective length raised by Shivashankar et al. to explore the water-debinding dynamics.[12] In addition, Krauss, Bakan, Park, Liang et al. have done some researches on different water-based binder systems with different kinds of powders.[17–20]. However, the practical production of injection-moulded ceramic parts with large section via partially water-debinding has seldom been reported and researched.

In this study, we adopt a combination of low molecular weight PEG (L-PEG) and high molecular weight PEG (H-PEG) as water-soluble binder to fabricate injection-moulded ceramic parts with large section, which has never been reported. The mechanism of the combination of PEG removal was proposed for the first time. Defect-free near gear parts with large-sized-section (thickness – 16 mm) were successfully fabricated through water extraction (15 h) followed by rapid thermal pyrolysis (4.5 h). It solves the difficulty of fabricating injection-moulded ceramic parts with large section and the approach is energy saving and high-efficiency as compared with conventional thermal debinding. The results demonstrate that our approach of partially water-debinding followed by rapid thermal pyrolysis could solve the problems of conventional thermal debinding, providing an effective route for the production of injection-moulded ceramic parts with large section.

Table 1
The used water-based binder system.

| Components | PEG | PMMA | SA | DBP | Phenothiazine |
|---|---|---|---|---|---|
| Weight percentage (%) | 66 | 20 | 8.5 | 5 | 0.5 |

## 2. Experimental procedure

The ceramic powder used was a commercial zirconia (3 mol% $Y_2O_3$) with average particle size ($d_{50}$) of 0.16 μm and Brunauer–Emmett–Teller specific area of 8 $m^2/g$ (grade YSZ-F-DM-3.0, Farmeiya Advanced Materials Co., Ltd., Jiujiang, China). The powders were mixed with the binders in a twin screw kneader (SK-160, ShangHai Rubber Machinery, Shanghai, China) at 150–170 °C for a period of 30–45 min. The binders used in water-based binder system for injection moulding in the experiments were: polymethyl methacrylate (PMMA, Plexiglas-8n, Degussa Co., Ltd., Beijing, China), polyethylene glycol (PEG) (Sinopharm Chemical Reagent Beijing Co., Ltd., Beijing, China), stearic acid (SA, Shantou Xilong Chemical Factory, Guangdong, China), dibutyl phthalate (DBP, Beijing Modern Eastern Fine Chemical) and phenothiazine (Sinopharm Chemical Reagent Beijing Co., Ltd., China) with the compositions shown in Table 1. At the same time, injection moulding using wax-based binder system was conducted simultaneously for contrast. The binders used in wax-based binder system for injection moulding were: polypropylene (PP, K8303, Beijing Yanshan Petrochemical Co., Ltd., China), ethylene–vinyl acetate copolymer (EVA, VA content was 14%, Beijing Chemical Factory, China), paraffin wax (Shenyang Paraffin-wax Chemical Co., Ltd., China), stearic acid (SA, Shantou Xilong Chemical Factory, Guangdong, China) and dibutyl phthalate (DBP, Beijing Modern Eastern Fine Chemical) with the compositions shown in Table 2.

The specimens were shaped using an injection moulding machine (JPH30C/E, Qinchuan Hengyi Plastics Machinery Co., Ltd., China). For water-based binder system, debinding was performed in two steps: water leaching to remove the PEG and thermal pyrolysis to remove residual binders. The green (as-moulded) specimens were immersed in distilled water which was held at 40 °C for the first stage. The second stage involved a thermal treatment. Because the pore nets first formed as a result of water debinding, heating rate of the second stage could be quite fast. For wax-based binder system, the as-prepared compact was debound for 48 h in air atmosphere in a muffle furnace.

After debinding, the compacts were finally sintered at a rate of 4 °C/min to 1000 °C and held there for 1 h and then sintered at a rate of 2 °C/min to 1500 °C and held for 2 h to finish sintering.

Table 2
The used wax-based binder system.

| Components | PP | EVA | PW | SA | DBP |
|---|---|---|---|---|---|
| Weight percentage (%) | 10 | 10 | 60 | 15 | 5 |

Table 3
The quality of the compacts of different compositions of PEG.

| Composition of PEG | PEG600 (100%) | PEG4000 (100%) | 66.7% PEG600 + 33.3% PEG4000 |
|---|---|---|---|
| Quality of the compacts | Poor stiffness | Crack, blistering | No defect |

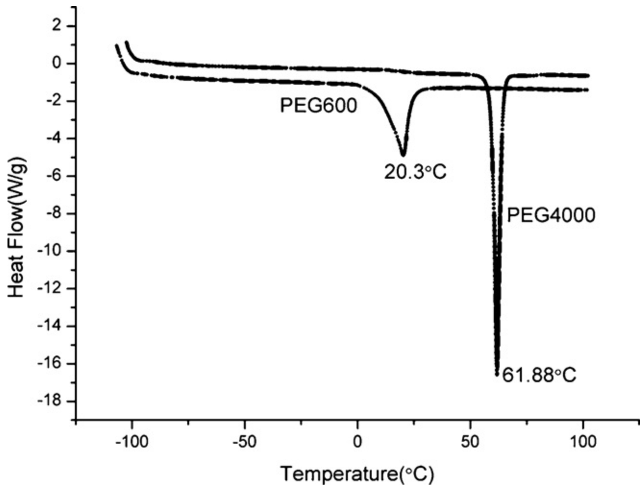

Fig. 1. The respective DSC curves of PEG600 and PEG4000 (note: 1 °C = 273.15 K).

## 3. Results and discussion

To justify the necessary combination of PEG, we have compared the effect of using L-PEG (alone), H-PEG (alone) and combination of PEG, the results of which are shown in Table 3. We adopt a combination of low molecular weight PEG (L-PEG) and high molecular weight PEG (H-PEG) as water-soluble binder to make a balance between the stiffness of the compact and the overcoming of swelling, because if H-PEG is adopted alone, it is quite easy for the compact to crack in water-debinding process with the swelling of H-PEG (fold chain) very obvious, while if L-PEG (linear chain) is adopted alone, it is difficult for the compact to maintain the shape. Therefore, 66.7% PEG600 + 33.3% PEG4000 is used as the water-soluble binder to fabricate large-section-sized injection-moulded ceramic parts via water-debinding. The DSC curve of PEG600 and PEG4000 is shown in Fig. 1 respectively, which indicates that the melting point of PEG600 is 20.3 °C while that of PEG4000 is 61.88 °C. The water temperature for water-leaching in our experiment is 40 °C, thus PEG600 is liquid while PEG4000 is folded chain crystal during water extract process. The mechanism of the combination of PEG removal in water bath could be explained as: (a) the chain segment of PEG600 could move freely for PEG600 is liquid at such temperature (40 °C). The removal rate of PEG600 is high and PEG600 could diffuse fast from the compact to the water solution. (b) After PEG600 removes at a fast rate at the first stage, some pores form around the molecular chain of PEG4000, which provides sufficient space for the swelling of PEG4000. Hence surface defects originated from swelling such as blistering (Fig. 2(a)) and crack (Fig. 2(b)) of the compact could be inhibited. It is just the superiority of using the combination of H-PEG and L-PEG. (c) Finally, both PEG600 and PEG 4000 are extracted from the compact to the water solution.

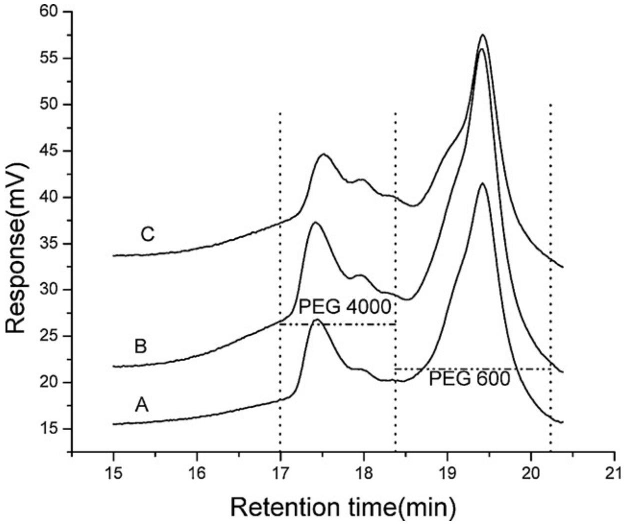

Fig. 3. Gel permeation chromatography (GPC) of the water solution (note: water extraction time: (A) 5 min, (B) 30 min, and (C) 6 h).

To verify the above model, we use gel permeation chromatography (GPC) to analyse the water extraction process (Fig. 3). The ratio of PEG600 to PEG4000 in the water solution could be calculated by MatLab Software and the results are shown in Table 4. At the initial stage of the water extraction process, the removal of PEG600 is more than that of PEG4000, leading to the ratio

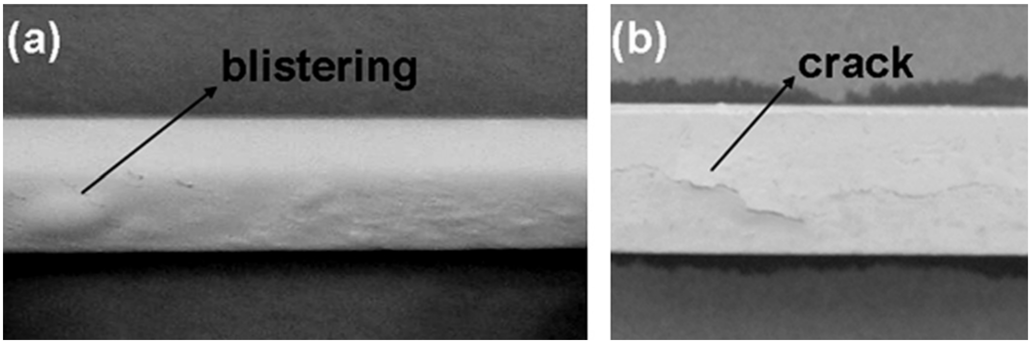

Fig. 2. (a–c) The mechanism of the combination of PEG removal in water bath; surface defects originated from swelling such as (d) blistering and (e) crack.

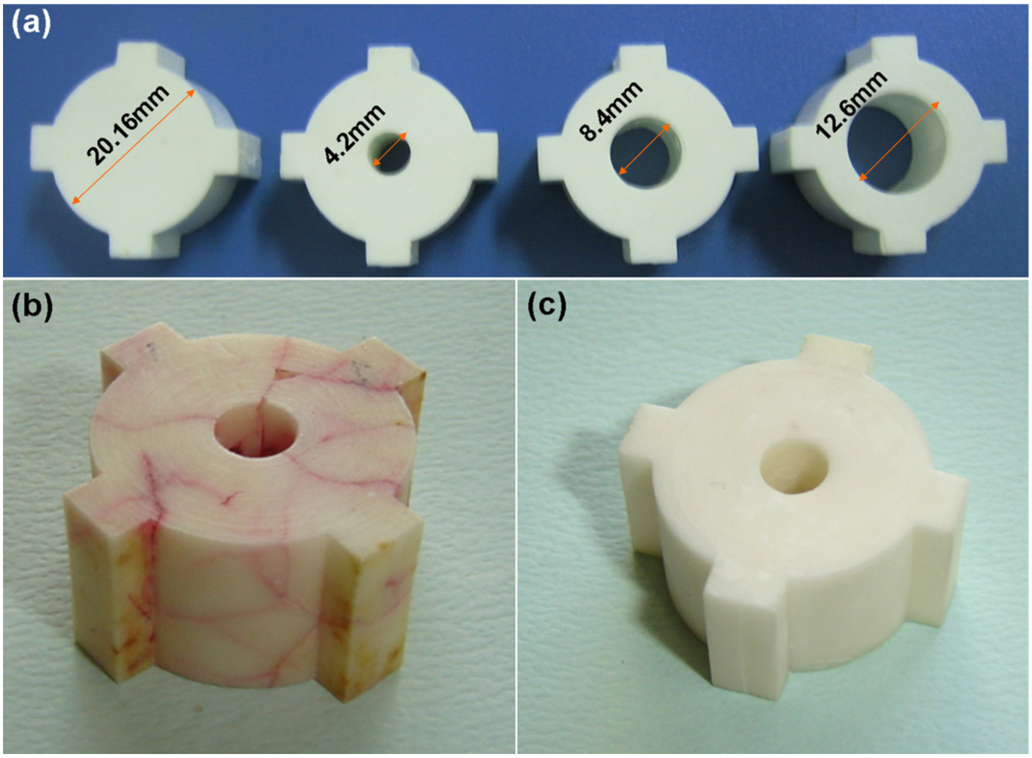

Fig. 4. (a) Injection-moulded near gear ceramic parts with different core sizes via our method; (b) near gear ceramic parts via thermal debinding; and (c) near gear ceramic parts partially water-debinding.

of PEG600 to PEG4000 higher than the ratio in the green body (compact without water extraction). As time elapses, the ratio of PEG600 to PEG4000 in the water solution decreases gradually according to Table 4. After 6 h of water extraction, the ratio of PEG600 to PEG4000 in the water solution is 2.35, which is close to the ratio in the green body. At this point, almost all the PEG in the compact removed into the water solution.

Fig. 4(a) corresponds to injection-moulded near gear ceramic parts with different core sizes via our method. It is obvious that large-section-sized (thickness – 16 mm) injection-moulded ceramic parts were fabricated successfully without any defect. Fig. 4(b) and (c) represents such near gear ceramic parts via thermal debinding and partially water-debinding respectively. The thermal debinding sample (Fig. 4(b)) experienced quite a long heating time (48 h) which is power-wasting and time-consuming. Nevertheless, surface cracks could still not be avoided as shown in the sintered body (the sintered body was immersed in red ink to make the surface cracks identified). By contrast, the partially water-debinding sample (Fig. 4(c)) experienced a short extraction time (15 h) followed by rapid thermal pyrolysis (4.5 h) which is energy-saving and high-efficiency. Furthermore, defect-free sample with large-sized-section could be successfully fabricated. It demonstrates that our approach of partially water-debinding could solve the problems of conventional thermal debinding, which provides an effective route for the production of large-sized ceramic parts.

Table 4
The ratio of PEG600 to PEG4000 in the water solution at different time intervals during water extraction process.

| Time | 5 min | 30 min | 6 h |
|---|---|---|---|
| PEG600/PEG400 | 2.91 | 2.68 | 2.35 |

*Note*: 1 min = 60 s, 1 h = 3600 s.

## 4. Conclusions

We adopt a combination of low molecular weight PEG (L-PEG) and high molecular weight PEG (H-PEG) as water-soluble binder to fabricate large-section-sized injection-moulded ceramic parts. The mechanism of the combination of PEG removal was proposed for the first time. We use 66.7% PEG600 + 33.3% PEG4000 as the water-soluble binder to prepare large-section-sized ceramic parts. Defect-free near gear parts with large section (thickness – 16 mm) were successfully fabricated through water extraction (15 h) followed by rapid thermal pyrolysis (4.5 h). It solves the difficulty of fabricating injection moulded ceramic parts with large-sized-section and the approach is energy saving and high-efficiency as compared with conventional thermal debinding. The results demonstrate that our approach of partially water-debinding followed by rapid thermal pyrolysis could solve the problems of conventional thermal debinding, which provides an effective route for the production of injection moulded ceramic parts with large section.

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