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New eco-friendly binder based on natural rubber for ceramic injection molding process

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ABSTRACT

The binder composition used for ceramic injection molding plays a crucial role on the final properties of sintered ceramic and to avoid defects on green parts. This study proposes a new eco-friendly binder based on natural rubber as a backbone polymer for ceramic injection molding of alumina. Three binders with different content of natural rubber and paraffin wax have been investigated. The powder volume fraction was kept constant. Physical properties were analyzed and four thermal debinding cycles on molded samples were applied for investigation of the influence of temperature and heating rate of sintered samples. All binders showed good rheological properties and yield stress was changed with homogeneity between powder-binder suspension. Thermal debinding affected the sintered properties of alumina samples. In result it was found that, between the binders used, the better binder components for injection process was obtained for 40% wt of natural rubber and 60% wt of paraffin wax.

1. Introduction

Ceramic injection molding (CIM) is a near-net shape processing technique that allows manufacturing of complex components in large scale industry. The CIM process involves the traditional shape-making capacity of plastic injection molding and the flexibility of materials employed in powder technology. The fabrication starts by compounding a polymeric binder and powder mixture, known as feedstock, followed by injection molding, binder removal and sintering [1,2].

The binder is a complex mixture comprising of several components, which is carefully selected to promote good injection molding properties and be easy for removal of molded parts. The primary component is a high molecular weight polymer which provides the adequate strength molded parts. The secondary binder component generally is a wax or low molecular weight polymer and acts to improve the rheological properties of feedstock, as well as easy removal of the binder. In this binder system, an excess of primary component may cause poor rheological properties, which increases the feedstock viscosity and implicates incomplete mold filling. On the other hand, low concentration of primary component can also lead loss of mechanical strength of molded parts.

Several binder systems were developed in the few last decades and the more traditional ones are based on thermoplastics, such as polypropylene (PP) and polyethylene (PE) blend for alumina injection molding [3], polyoximethilene for μPIM of stainless steel 316L powder (POM) [4]. Thermosetting binders based on epoxy were patented by Nishimura and Yoshino [5].

More recently binders based on water-soluble polymers have been developed. Weil et al. [6] developed the ethylene vinyl acetate (EVA) binder for injection molding of Ti–6Al–4V alloy, giving a maximum powder loading of 65% vol. The starch-based binder and low density polyethylene (LDPE) was used with stainless steel 316L by Abolhasani and Muhammad [7]. An eco-friendly binder composed by polyethylene glycol (PEG) and cellulose acetate butyrate (CAB) for zirconia injection molding was developed by Abajo et al. [8].

This paper proposes the development of a new eco-friendly binder for the powder injection molding (PIM) process based on natural rubber latex as backbone polymer and paraffin wax as a secondary component. The aim of development of this binder is the study of natural rubber as a backbone binder component for CIM process. This is obtained from the *Hevea brasiliensis* tree, a renewable natural source, and has not been used yet as binder in

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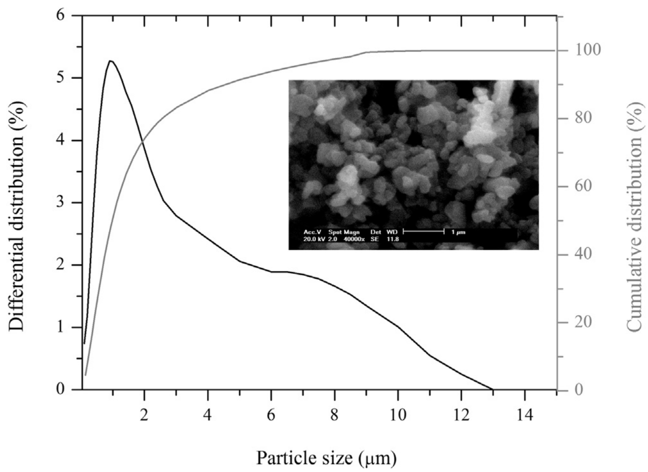

Fig. 1. Particle size distribution of alumina A16-SG with a SEM image showing an irregular particle shape.

CIM process. Likewise this natural rubber has beneficial properties, its elasticity can help the demolding step of complex and thin parts. The influence of paraffin wax and natural rubber content on the rheological properties, thermal stability and sintered alumina properties were analyzed, as apparent density, linear shrinkage and flexural strength.

2. Experimental procedure

2.1. Powder

Alumina powder of commercial purity (A 16-SG) was used in this research. This powder was supplied by Almatis. Powder morphology was observed in a scanning electron microscope – SEM (Philips XL 30), and particle size distribution was measured using a laser scattering particle analyzer (Cilas 1064L).

The powder has a particle size distribution with a d_{90}, d_{50}, d_{10} and average diameter of 4.51, 0.94, 0.19 and 1.71 μm, respectively. Particle size distribution curves are presented in Fig. 1 with a SEM image showing irregular shape of the particles.

2.2. Feedstock systems and compact molding

The backbone polymer of binder is composed of natural rubber latex (NR) as the primary component and used directly as extracted from the tree (*H. brasiliensis*), from Thailand, stabilized by addiction of ammonium hydroxide solution, and supplied by the Thai Rubber Public Company Ltda. Paraffin wax was used as a secondary binder component (PW – supplied by Farmaquímica, Brazil), stearic acid 95% (supplied by VETEC, Brazil) and dicumyl peroxide 98%, (supplied by Sigma–Aldrich, Germany). Table 1 describes the function and properties of binder components.

The effect of natural rubber latex (NR) and paraffin wax (PW) content of the binder on the thermal and rheological behavior of composition and sintered properties of samples was analyzed. The content of both components are described in Table 2, as well as the injection parameters used for sample molding. Stearic acid and dicumyl peroxide concentration in all feedstock was kept at 11% wt and 5% wt, respectively.

The feedstocks were prepared using mechanical stirring at 100 rpm to homogenize the suspension with water as a medium. NR latex suspension (60% wt of solids), PW and SA were mixed at 90 °C. After all the PW and SA were melted, dicumyl peroxide and alumina powder was added. The feedstock was continually stirred at 100 rpm and heated at 90 °C until the feedstock was dry. Finally, the feedstocks were kept in an oven at 40 °C for 24 h to remove any remaining water.

The feedstocks were molded into a mini-injection molding machine (Haake II, Thermo Scientific). The injection molding parameters used for molding the samples was listed in Table 2. These parameters were selected based on preliminary tests that evaluated the surface integrity of molded part. The as-moulded compact shape is shown in Fig. 2. Five samples were made for each feedstock composition. The temperature of barrel was kept at 85 °C in order to prevent premature vulcanization. The samples were vulcanized in the mold at 160 °C for 1 min. A drawback of this binder during the injection molding is that the feedstock cannot be reused after molding.

2.3. Debinding and sintering

For binder removal only the thermal degradation method was used and its effect on sintered properties was investigated. Four thermal debinding cycles were used, as listed in Fig. 3. The thermal debinding cycle 1 used the heating rate of 0.2 °C min^{-1} until the temperature of 300 °C, debinding cycle 2 heated at a rate of 0.1 °C min^{-1} until the 300 °C isothermal temperature, and the debinding cycles 3 and 4 used 0.2 °C min^{-1} to isothermal temperature of 400 and 500 °C, respectively. It was kept at isothermal temperatures to 60 min for all samples.

Each thermal binder removal cycle used five samples. After debinding, the samples were heated at 10 °C min^{-1} to 1000 °C and kept constant at this temperature for 1 h for pre-sintering of samples. No procedure of surface finishing, such as grinding or polishing, were applied to pre-sintered samples. Finally the samples were sintered at 1650 °C for 1 h (furnace Inti/MaitecMEV1700/V).

Table 1
Physical properties of binder components.

Binder component	Chemical structure	Melting point (°C)	Density (g cm^{-3})	Function
Natural rubber (NR)	$(C_5H_8)_n$	–	0.96	Backbone (secondary component)
Paraffin wax (PW)	$(C_nH_{2n+2})_n$	60–62	0.90	Primary component
Stearic acid (SA)	$C_{18}H_{36}O_2$	65–68	0.94	Surfactant
Dicumyl peroxide	$[C_6H_5C(CH_3)_2]_2O_2$	39–41	1.56	Crosslinking agent

Table 2
Designations of feedstock formulation and injection molding parameters of feedstock composition.

Feedstock code	NR (wt%)	PW (wt%)	Powder loading% vol. (wt%)	Injection molding parameters			
				Injection pressure (bar)	Hold pressure (bar)	Barrel temperature (°C)	Mold temperature (°C)
50NR/50PW	50	50	56 (83.93)	300	210	85	160
40NR/60PW	40	60	56 (83.93)	200	140	85	160
33NR/67PW	33	67	56 (83.93)	150	100	85	160