



Thermal stability and degradation kinetics of feedstocks for powder injection moulding – A new way to determine optimal solid loading?

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ABSTRACT

Degradation kinetics and the thermal stability of zircon powder injection moulding feedstocks (PIM) based on cellulose acetate butyrate (CAB) and polyethylene glycol (PEG) binders were investigated using simultaneous thermogravimetric analysis (STA). The initial decomposition temperature (IDT) and the integral procedure decomposition temperature (IPDT) were used to analyse the thermal stability of the binder system as a function of the solid loading content. The degradation kinetics was studied, and the degradation activation energy was assessed for varying zircon powder contents using isoconversional methods. All the methodologies revealed changes in the thermal degradation behaviours of the feedstocks for solid loadings that were previously determined to correspond to optimal solid loadings using other experimental procedures. These results may promote the proposal of thermodynamic degradation studies of feedstocks as an alternative or complementary technique to determine optimal solid loading contents in powder injection moulding (PIM). The studies in this paper also examined PIM process operation temperatures for zircon feedstocks.

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1. Introduction

Powder injection moulding (PIM) is one of the main manufacturing processes used to produce small parts with complex geometries, thin walls and in large production batches [1,2]. This technology is applied to a wide variety of ceramics, metallics and combinations thereof [3]. The process consists of mixing a fine powder material with different polymer-like compounds, the so-called binder system. The binder system provides sufficient fluidity to the newly created feedstock to allow mould filling during injection and easy removal during the subsequent debinding process. The binder system must be added in such quantities so as to optimise the process conditions and time required. The volume occupied by the binder decreases during debinding, and the density of the powder particles increases during sintering to achieve the final part properties. Shrinkage occurs as consequence of sintering. To minimise shrinkage and increase part tolerances, the maximum powder volume fraction is desired. This powder particle fraction is limited by rheological factors and by technical considerations during debinding. The particle volume fraction ranges from 50 vol.% to approximately 70 vol.%, depending on the powder and binder

characteristics. At present, the optimal solid loading is determined by rheologic measurements and the final part properties.

Currently, there are various sophisticated methods of eliminating polymeric components of the feedstock, but debinding normally requires two consecutive stages. First, one of the binder components is removed by a physical solvent process that creates interconnected channels to facilitate the removal of volatiles during a second thermal debinding stage. This procedure not only prevents defects by relieving the internal pressure from any trapped volatiles but also allows a more rapid elimination of volatiles than a single thermal step process. Powder particles constitute a barrier for both polymer chains that are removed by solvent and volatile products resulting from thermal degradation, which limits the effectiveness of the debinding. Moreover, during thermal debinding, atmospheric and temperature conditions are important considerations. For typical polymer decomposition temperatures, the probability of material contamination with elements such as carbon or oxygen becomes especially important for metallic materials. Therefore, a thermal debinding process preferably uses an inert atmosphere whenever possible, although oxygen is more effective for organic component degradation.

Polymer decomposition mechanisms within the feedstock are very complex. The decomposition of a single binder component by itself is complex, as in PEG decomposition in an inert gas. Polyethylene glycol (Fig. 1b) is a polyether compound formed by the polymerisation of ethylene oxide monomers with conforming

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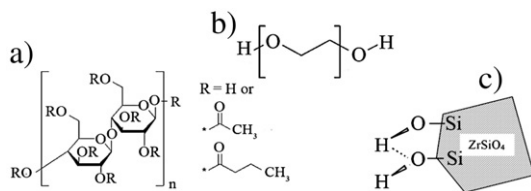


Fig. 1. The chemical structures of the different feedstock components: a) the basic cellulose acetate butyrate monomer and possible substitution groups; b) poly(ethylene glycol) monomer and end chain hydroxyl groups; and c) a representation of the hydroxyl groups on the zirconium silicate particle surface.

linear chains. There is extensive literature describing the thermal degradation of PEG in terms of the decomposition of volatiles or the pyrolysis of by-products studied with chromatography, infrared spectroscopy or mass spectroscopy [4,5]. The products obtained during PEG pyrolysis include various formaldehydes, acetaldehydes, ethylene glycol, ethylene oxide, water, low-carbon alkenes, carbon monoxide and dioxide and traces of other low molecular weight hydroxyl, carboxyl, carbonyl and ethereal compounds. The decomposition of CAB, an ester of cellulose that includes not only its main constituent monomers (beta-D-glucose chains) but also variable substitution of butyryl, acetyl and hydroxyl side groups, results in even more complex products (Fig. 1a). Cellulose pyrolysis has been studied for more than six decades. Even so, the molecular-level processes underlying the pyrolysis reactions remain poorly understood. Gongwer et al. detected carbon monoxide, carbon dioxide, methyl acetate and methyl butyrate among the volatile fractions derived from CAB pyrolysis with certain amounts of ketenes and ethyl ketenes, butyric and acetic acid [6]. That study showed the complexity of the products that presumably result from feedstock degradation. On the one hand, the findings indicate the probable influence of the different interactions among constituents on the global decomposition behaviour. Zirconium silicate surface and hydroxyl groups (Fig. 1c) most likely interact with side or end groups present in the CAB and PEG chains. On the other hand, degradation compounds from the less thermally stable polymers may also affect the onset temperature of the most thermally stable polymer. Furthermore, particles act as a barrier to the removal of volatiles and, thus, affect the degradation rate.

In this work, simultaneous calorimetry and thermogravimetric analyses were performed to study the thermal decomposition of zirconium silicate feedstocks composed of cellulose acetate butyrate (CAB) and polyethylene glycol (PEG) binders in an inert nitrogen atmosphere. Binder and feedstock temperature stability and decomposition kinetics were investigated using integral procedure decomposition temperature (IPDT) and isoconversional methodologies, respectively. Several isoconversional methods were used, and their convenience is discussed. The FTIR technique was used to investigate possible interactions between feedstock components.

Several zirconium silicate feedstocks consisting of mixtures with different proportions of constituents were investigated; these variations allowed the effect of the effective powder surface on the chemisorption of CAB and PEG molecules and the channel volume used to remove volatiles to be elucidated. The degradation of the binder system was studied to evaluate the extent of the influence that particles exert on the decomposition of CAB and PEG. The results reveal changes in the thermal degradation behaviour with solid loading. Based on the findings, a method to determine the optimum solid loading conditions using thermogravimetric tools is proposed and discussed.

2. Experimental

Zirconium silicate powders were supplied by GUZMÁN GLOBAL S.L. (Nules, Spain) and exhibit an irregular, edged morphology. A

Malvern 2000 laser scattering device was used to measure the particle distribution parameter. The particle size parameters (D_{50} and D_{90}) are 1604 and 465 μm , respectively. The powders have a specific surface area of 5.0363 m^2/g , as measured with a Micro-metrics Gemini VII BET measurement device.

A binder system based on PEG and CAB was selected. These binders have been demonstrated to be effective for zircon PIM and provide improved properties when compared to other binder systems [7]. However, there are no published comprehensive studies on their thermal degradation. The binders consist of two types of CAB: CAB381-0.1 and CAB551-0.01. Each of these binders has different percentages of butyryl, acetyl and hydroxyl groups blended with two types of PEG with different average molecular weights. The composition of the binder system and the characteristics of the components are shown in Table 1.

A Rheomix 600 Haake rheometer coupled with a Haake Rheocord 252p module was used for the mixing experiments. Different feedstock compositions, ranging from 0 vol.% zircon powder (single binder) to 52.5 vol.% (minimum solid loading tested) to 65 vol.%, were investigated in 2.5 vol.% increments. A temperature of 150 $^{\circ}\text{C}$ was used for all the batches, and the mixing chamber was filled with feedstock to 72% of the total volume (the chamber volume is 69 cm^3). A rotor speed of 50 rpm was employed to mix the feedstock and the binder for 60 min to ensure complete homogenisation. In addition, a batch was produced by dissolving all of the binder components in an ethylene acetate solvent and placing it in a vacuum at 120 $^{\circ}\text{C}$ for 8 h to ensure maximum homogenisation of the polymer components.

A Perkin Elmer STA 6000 device was used to thermodynamically evaluate the decomposition of the binder and the feedstock. This device allows the simultaneous acquisition of the thermogravimetric TGA curves and the DTA/DSC curves. The examined temperature range was from 50 $^{\circ}\text{C}$ to 650 $^{\circ}\text{C}$. Calcium oxalate was employed for thermogravimetric calibration, whereas elemental indium (99.999% pure) was used for heat and temperature calibration. An inert nitrogen atmosphere was employed with a flow rate of 40 ml/min. Feedstock pellets of approximately the same morphology and weight were used for the analysis. The net weight of the binder in the feedstock was constant for all experiments, with a minimum of 5 mg for all cases. For a thorough evaluation of the decomposition kinetics, four heating rates were evaluated: 10 $^{\circ}\text{C}/\text{min}$, 15 $^{\circ}\text{C}/\text{min}$, 20 $^{\circ}\text{C}/\text{min}$ and 25 $^{\circ}\text{C}/\text{min}$.

A Philips XL 30 scanning electron microscope (SEM) and an Olympus GX71 light optical microscope (LM) with a polarised filter were used to determine the homogenisation. Fourier transform infrared spectroscopy (FTIR) measurements were recorded using a Perkin Elmer Spectrum GX device.

3. Results

3.1. Thermal degradation of binder in N_2

Fig. 2 presents typical differential scanning calorimetry curves (DSC), thermogravimetry (TG) curves (or thermograms) and the derivative of the TG curves (DTG) for feedstocks in a nitrogen

Table 1
Composition of the binder material.

	CAB381-0.1	CAB551-0.01	PEG20k	PEG4k
Vol.%	10	30	58	2
T_{MELT} [$^{\circ}\text{C}$]	155–165	127–142	63–66	58–61
T_{GLASS} [$^{\circ}\text{C}$]	123	85	<0	<0
M_w	20,000	16,000	20,000	4000
Supplier	Eastman	Eastman	Aldrich	Aldrich

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