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Decomposition of binder from a ceramic injection molding sample

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Abstract

Ceramic injection molding (CIM) has been recognized as attractive technique for the fabrication of ceramic parts. Binder systems comprise between approximately 5 and 40 vol.% of a given ceramic green body depending on the chosen forming method. In this work, the thermal decomposition behaviors of four binder systems used in CIM were investigated by thermal analysis. The decomposition kinetic parameters were also evaluated using non-isothermal DSC/TG techniques. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ceramic injection molding; Thermal analysis; Kinetic parameters

1. Introduction

The processing of ceramic green body involves using polymeric binders consisting of distinct attributes to blend with ceramics powders forming a flow, uniform suspension so that the mixture can be shaped into a prescribed mold cavity at a given set of temperature and molding variables [1]. The binder formulation, in particular, has previously received more attention mainly because an ideal binder system suited for all different powder characteristics is still impossible to attain and an inevitable restriction would accordingly be imposed onto the process window from the selection of binder composition. The organic binder system used in ceramic injection molding usually consists of a major binder, a minor binder, a plasticizer or a lubricant, a wetting agent and a dispersant for processing ceramic powders [2].

Those additives that remain in the as-formed ceramic body after drying are transient aids that must be removed completely prior to component densification at elevated temperature. This process is known as binder removal [3–6]. In this work, a zirconia-binder mixture containing different compositions of binder was first injection-molded. The decomposition behaviors and the decomposition kinetic parameters were then investigated by non-isothermal TG/DSC techniques.

2. Experimental

Blends containing zirconia powder (HSY3.0, Daiichi, Japan) having an average size of ~0.25 μm, paraffin wax, polymeric resin, and acid were prepared using ball milling in a polyethylene jar with methyl ether ketone as liquid medium. The zirconia was fixed at 50 vol.% and the organic vehicle consisting of the paraffin wax, polymeric resin, and stearic acid was

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Table 1
Composition of ceramic mixtures

Ceramic-mixture No.	Binder composition (wt.%)			
	Zirconia	Stearic acid	Paraffin wax	Vinyl acetate polymer
SA15	86.7	0.9	7.0	5.4
SA30	86.7	1.7	6.5	5.1
SA45	86.7	2.6	6.0	4.7
SA75	86.7	4.3	5.0	3.9

fixed in the approximate weight ratio. The wax ($T_m \sim 67°C$) and the stearic acid ($T_m \sim 70°C$) are defined as the low-melting component and the resin ($T_m \sim 150°C$) as the high-melting component. The compositions of ceramic mixture are listed in Table 1. After oven drying at 40°C, the resultant blends were further mixed and compounded in an extruder (Model 70–20 vex-6, KCK Industrial, Japan) using a barrel temperature (feed to exist) of 100–120–140–170°C and were granulated.

The prepared blends were shaped into MOR bars with dimensions of 45 mm × 5 mm × 5 mm by injection molding (Battenfeld, Model BA 250/50 CDC, Germany) with a barrel temperature from feed to nozzle of 90–120–140–160–175°C. The injection pressure was 50 MPa and the mold temperature was 45°C. Part of the MOR bar were sliced carefully using a thin blade. Sample for experiment runs were taken as ~50 mg from each of the sliced sections and DTA/TG measurements were conducted using a thermal analyst Du-Pont 2000 series with equipped and 951 DSC cell and a 950 TG unit. Measurements were carried out in static air atmosphere at a heating rate from 5 to 30°C min^{-1}.

3. Results and discussion

Thermal analysis techniques, particularly differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), have proven useful for evaluating kinetic parameters of various reactions and materials [7–9], DSC methods [7] are often quite straightforward. Kinetic parameters have been derived based on the peak temperature–program-rate relationship. The most straightforward DSC method is based on the variable program rate method of Ozawa [10] and has been evaluated for use with industrial materials. This method is reasonably rapid accurate and applicable to many materials. It is the basis of an ASTM technique developed by committee E27 on hazard potential of chemicals (ASTM method E698). An alternative method for determination of activation energy is that described by Kissinger [11].

$$\frac{\mathrm{d}\,\ln(h/T_p^2)}{\mathrm{d}(1/T_p)} = \frac{-E}{R} \tag{1}$$

where E is the activation energy (kJ mol^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}), h the program rate (°C min^{-1}), T_p the peak temperature (K). A series of sets of program rate and peak temperature data was generated, and activation energy was calculated by plotting log program rate $[\log(h/T_p^2)]$ versus the reciprocal peak temperature.

Ozawa [10], Flynn [12] and Doyle [13] have shown that activation energy of a thermal decomposition process can be determined directly from a series of TG curves obtained at different heating rates. The method developed by Flynn is a quick, simple method for determining activation energies directly from mass loss versus temperature data at several heating rates. It is not to be expected that any single kinetic expression would be applicable to a wide range of decomposition process. A kinetic analysis method based on the assumption that the decomposition obeys first-order kinetics was later generalized. The Arrhenius activation energy is determined from a plot of the logarithm of heating rate versus the reciprocal of the absolute temperature at constant conversion level. The slope of these plots with an average value of 0.457 is used in the following equation:

$$\frac{\mathrm{d}\log(h)}{\mathrm{d}(1/T)} = -\left(\frac{0.457}{R}\right)E \tag{2}$$

Table 2
Activation energies for the thermal decomposition of four CIM binder systems as evaluated by non-isothermal techniques

Mass loss (%)	SA15		SA30		SA45		SA75	
	E_a (kJ mol^{-1})	$-r_a$	E_a (kJ mol^{-1})	$-r_a$	E_a (kJ mol^{-1})	$-r_a$	E_a (kJ mol^{-1})	$-r_a$
1	68	0.9861	67	0.9594	65	0.9976	69	0.9865
3	69	0.9876	68	0.9832	79	0.9874	82	0.9961
5	64	0.9868	73	0.9733	78	0.9883	78	0.9897
7	67	0.9975	75	0.9673	74	0.9892	67	0.9801
9	65	1	76	0.9745	73	0.9869	79	0.9893
11	65	0.9984	74	0.9931	67	0.9785	75	0.9964
13	67	0.9993	75	0.9765	59	0.9865	73	0.9796
Dynamic DTA	87	0.9746	63	0.9865	70	0.9775	79	0.9643

The value of 0.457 is was obtain using a series of iterations. The value of E/RT was calculated where E is the approximate activation energy and T is the temperature obtained using a program rate near the middle of the range at a constant mass loss (nominally 10°C min^{-1}).

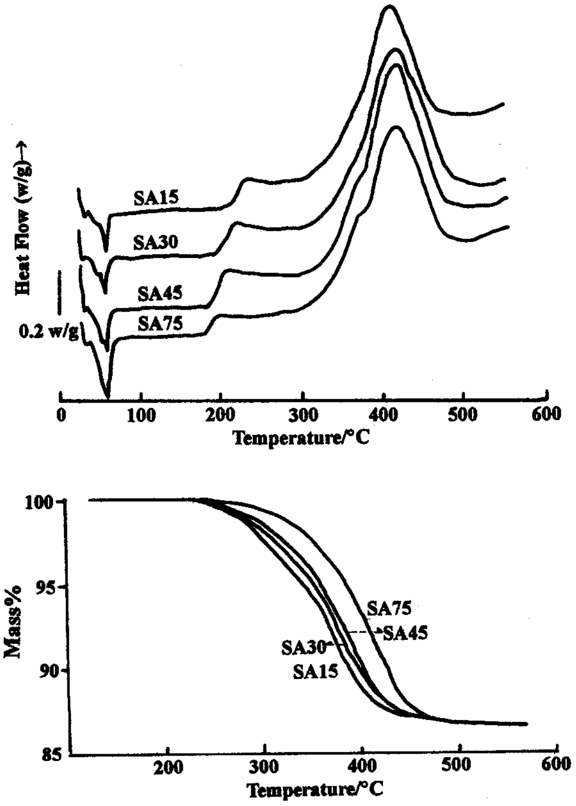

Fig. 1. TG/DSC curves of four CIM binder systems.

Table 2 contains the activation energies of decomposition for four binder systems used in CIM that were evaluated by non-isothermal techniques. Although the compositions of binder systems are different the activation energies for the decomposition of the four binder systems are very similar. The activation energies for decomposition of the four binder systems ranged from 59 to 82 kJ mol^{-1} as determined by dynamic TG methods.

TG and DSC curves for the four binder systems are displayed in Fig. 1. The DSC curves contained a broad endothermic peak around 50–70°C which reflects the melting point of the combined stearic acid and paraffin wax, and an extremely broad exothermic peak which ranged from 200 to 500°C corresponds to the decomposition of stearic acid, paraffin wax and polymer. TG analysis revealed a corresponding mass loss when the sample was heated to 500°C at an appropriate rate. This mass loss was substantially reduced as the level of low molecular weight constituents was increased. Similarly the temperature at which the maximum mass loss occurred also decreased proportionally to the amount of stearic acid present.

4. Conclusion

The thermal decomposition behavior of the four binder systems for CIM has been characterized. The binder decomposition for green body forms can be sketched using TG/DTA/DSC. Furthermore, the thermal analysis data and the physical properties of the green body may be utilized to select, a suitable binder removal procedure (time and temperature), and to suggest the best thermal debinding conditions. The kinetic parameters for the decomposition of the four binder systems have been evaluated using non-isothermal techniques. The apparent activation energies ranged from 59 to 87 kJ mol^{-1}.

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