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The thermal decomposition behaviors of stearic acid, paraffin wax and polyvinyl butyral

Kuen-Shan Jaw[a,*], Chung-King Hsu[b], Jinn-Shinng Lee[c,d]

[a]*Department of Chemical Engineering, Kuang Wu Junior College of Technology, Peito, Taipei, Taiwan, ROC*
[b]*Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC*
[c]*Department of Chemistry, Chung Yuan Christain University, Chungli 32023, Taiwan, ROC*
[d]*PO Box 90008-15-9, Chung Shan Institute of Science and Technology, Lungtan 32526, Taiwan, ROC*

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Abstract

Organic processing additives, such as polymers, dispersants, solvents and plasticizers, are often required to enhance the forming capabilities of ceramic powders. The term binder system is used to collectively describe those added materials that remain in the as-formed ceramic body after drying. Such additives must then be removed completely prior to component densification during subsequent different heat treating procedures. In this work, the thermal decomposition behaviors of binder system such as stearic acid, paraffin wax and polyvinyl butyral were investigated using DTA/TG. The kinetic parameters of thermal decomposition were also evaluated by non-isothermal DTA/TG techniques. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermal decomposition; Stearic acid; Paraffin wax; Polyvinyl butyral

1. Introduction

Binder systems provide many properties useful in ceramics processing such as green strength, dispersion mold release, etc. Polymer additives enhance the strength of green bodies by binding the ceramic particles together [1–8]. Additives from oleic acid or stearic acid are often used to improve ceramic powder dispersion during mixing [9–10]. Although binder systems are good for ceramic processing, a subsequent de-binding process is necessary to remove the binder vehicle, and the binder chemistry has been reported not only to influence the suspension rheology, but also to critically affect the integrity and shape retention of moldings. In this work, the thermal properties and the kinetic parameters of the decomposition for polyvinyl butyral (PVB), stearic acid and paraffin wax were investigated using DTA/TG and non-isothermal techniques.

2. Experimental

Low molecular weight of polyvinyl butyral, paraffin wax manufacturing by Gin-Ming Chemical, Taiwan and stearic acid manufacturing by Lancaster, USA, average molecular weight of 284.5 g mol^{-1} and melting point of 67°C are used in this work. Differential thermal analysis and thermogravimetry analysis (DTA/TGA) were conducted on the thermal analyst 2000 (E.I. Du Pont de Nemours, USA). A small

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[*] Corresponding author.

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amount of the sample (10–15 mg) was used, the test conditions were conducted in static air and operated at a heating rate from 5 to 30°C min^{-1}.

3. Results and discussion

The decomposition of these materials was investigated using DTA and DSC techniques. In order to analyze the kinetic parameters of decomposition, the Kissinger plot approach [11,12] proposed for usual chemical reactions, has been applied using non-isothermal techniques. From this, the kinetic parameters of decomposition can be calculated from a set of DTA/DSC curves, but the assumptions for each equation should be briefly described before using the following equations:

$$\ln h = -\frac{E_a}{RT_p} + \text{const.} \tag{1}$$

$$\ln\left(\frac{h}{T_p{}^2}\right) = -\frac{E_a}{RT_p} + \text{const.} \tag{2}$$

where h is the heating rate (°C min^{-1}), T_p the exothermic peak temperature of DTA/DSC curves, E_a the activation energy of decomposition of the materials, R the gas constant. These are calculated using a non-isothermal DSC method and are listed in Table 1.

Flynn and Wall [13], Doyle [14], et al. have illustrated that the activation energy of a thermal decomposition process can be determined directly from a series of TG curves which are carried out at different heating rates. The method that was developed by Flynn et al. was quick and simple for determining activation energies directly from mass loss vs. temperature data at several heating rates. They define the degree of conversion, C, the residual fraction, is equal to the weight of material loss divided by the total weight loss when T or $t \to \infty$. The thermogravimetric rate is given by

$$\frac{dC}{dt} = \left(\frac{A}{h}\right) f(c) \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where T is the absolute temperature, h the constant heating rate, A the pre-exponential factor of the Arrhenius equation, E_a the activation energy, R the gas constant, and $f(c)$ a function of degree of conversion (mass loss). If $A, f(c)$, and E are independent of T, then A and E are also independent of C. By utilizing the successive approximation method, the approximate activation energies have been determined. The constant in Eq. (4) may be easily recalculated and the correct activation energies can be obtained. For $20 \leq E/RT \leq 60$, the slopes that average to 0.457 are used in Eq. (4) and varies as ±3%.

$$\frac{d(\log h)}{d(1/T)} = -\left(\frac{0.457}{R}\right) E_a \tag{4}$$

Fig. 1 shows TG and DTA curves of polyvinyl butyral, stearic acid and paraffin wax. In TG curves,

Table 1
Activation energies of decomposition for stearic acid, paraffin wax and polyvinyl butyral evaluated by non-isothermal techniques

Mass loss (%)	Stearic acid		Paraffin wax		Polymer	
	E_a (kJ mol^{-1})[a]	$-r_a$[b]	E_a (kJ mol^{-1})	$-r_a$	E_a (kJ mol^{-1})	$-r_a$
5	92	0.9995	116	0.9945	138	0.9857
10	82	0.9867	90	0.9885	152	0.9734
20	76	0.9868	103	0.9768	155	0.9670
30	73	0.9840	88	0.9595	167	0.9492
40	71	0.9889	96	0.9774	193	0.9768
50	70	0.9906	102	0.9904	177	0.9921
60	71	0.9934	105	0.9922	160	0.9863
70	70	0.9963	110	1.000	218	0.9727
80	71	0.9972	118	0.9961	260	0.9943
90	78	0.9983	117	0.9984	371	0.9873
Dynamic DSC	81	0.9895	120	0.9957	145	0.9786

[a] Activation energy of decomposition.

[b] Correlation coefficient.

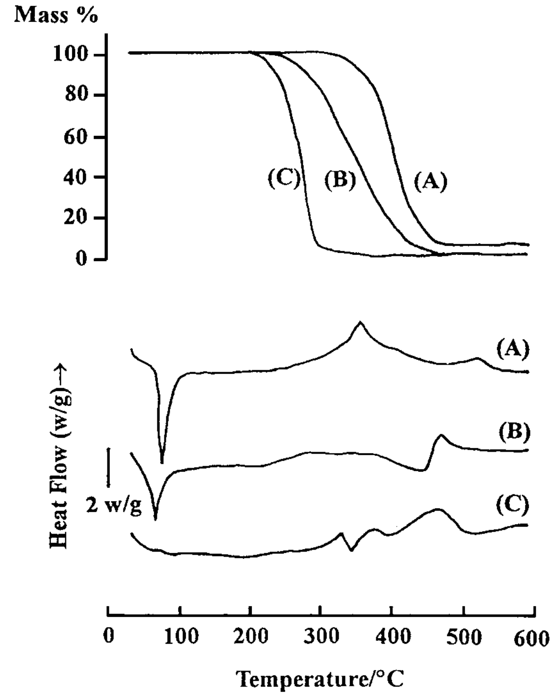

Fig. 1. TG/DSC curves of (A) stearic acid, (B) paraffin wax and (C) polyvinyl butyral.

above 160, 210 and 300°C, the stearic acid, paraffin wax and polyvinyl butyral start to decompose, respectively, the temperature range of decomposition stage is very broad, and the mass loss percentage of the three materials tend to 0% at higher temperature, which is the ideal case for binder removal in ceramic processing. In DTA curves, stearic acid shows a sharply endothermic peak at 67°C, which is the melting point of stearic acid, and then accomplished a broad exothermic peak at the temperature range of 360–380°C, and a small exothermic peak appeared at 515°C. Paraffin wax also shows an endothermic peak at 60°C, which is the melting point of paraffin wax. Then a broad exothermic peak appeared at 450°C. But there is only an unclear endothermic peak at low temperature, which indicates that the loss of water and volatile, relatively broad exothermic peak (ranges from 350 to 510°C) is following the melting of polyvinyl butyral. This result indicated that polyvinyl butyral undergoes multi-step degradation processes. From the point of view that the mass loss percentage of the three materials at higher temperature tend to 0%, the result of the TGA measurements seem to contradict the good binder burnout result.

The kinetic parameters of decomposition for stearic acid, paraffin wax and polymer are estimated by applying the technique of dynamic thermogravimetry, and the activation energies of decomposition for stearic acid, paraffin wax and polyvinyl butyral are evaluated by dynamic TG method listed in Table 1.

It has to be considered that the initial portion of the TG curves can be fitted with first-order reaction equation. In this work, we recognized that the activation energy can be evaluated using the Arrhenius equation at a lower mass loss in TG curve. Mass loss was consistently lower than 20%, and the decomposition activation energies of stearic acid under static air atmosphere are 76–92, 90–116 kJ mol^{-1} for paraffin wax and 138–155 kJ mol^{-1} for polyvinyl butyral, and the activation energies of decomposition with the mass loss percentage larger than 20% are also listed in Table 1. The activation energy of decomposition of stearic acid and paraffin wax did not change significantly. But the activation energy of decomposition of polyvinyl butyral increased with increasing mass loss, and the higher the mass loss increased. This indicated that the thermal behaviors of polymer play a major role of binder removal, and in this work, the activation energies of decomposition for stearic acid, paraffin wax and polyvinyl butyral that evaluated by non-isothermal DSC and dynamic TG method are very close.

Fig. 2 shows the surface microstructure of sample during the preparation of ceramic injection molding and after heat-treatment procedures. The surface microstructure is quite uniform with no crack. It

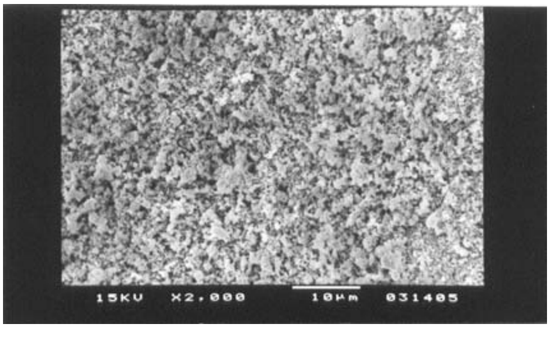

Fig. 2. Surface microstructure of zirconium oxide sample after a heat-treatment procedure.

has been sure that the heat treatment procedures of CIM sample are suited for binder removal.

4. Conclusion

The term binder system is used to collectively describe those additives that remain in the as-formed ceramic body after drying. Such additives are transient aids that must be removed completely prior to component densification at elevated temperature. The experiments proved that the binder system composite consisting of stearic acid, paraffin wax and polyvinyl butyral would show good thermal behavior in ceramic processing, and the binder system would burnout at considerably low temperature. Moreover, this effect is advantageous for the binder burnout procedure and it ensures that the removal of binder is easy.

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