EFFECT OF GLASS TRANSITION TEMPERATURE OF POLYMERIC BINDERS ON PROPERTIES CERAMIC MATERIALS

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Abstract

In the paper are presented the studies of the effect of glass transition temperature of new water-thinnable polymeric binders on the properties of ceramic materials obtained by die pressing. The parameters of ceramic samples comprising polymeric binders have been compared with those of samples comprising poly(vinyl alcohol) (PVA) – water-soluble binder. When using poly(acrylic-styrene) (AS), poly(acrylic-allyl) (AA) and poly(vinyl-allyl) (VA) water-thinnable binders, materials of greater density and mechanical strength were obtained in the green state as well as after sintering than those in the case of using PVA. The dependence of the chemical structure of the binders applied on the properties of samples such as the glass transition temperature and hydrophobic–hydrophilic balance of the copolymers has been discussed.

Keywords: alumina, die pressing, DSC, glass transition temperature, polymeric dispersions, PVA, Weibull modulus

Introduction

In modern ceramics, different polymeric binders of various chemical structure are applied for different molding methods. A narrow range of water-soluble organic binders, such as poly(vinyl alcohol) and poly(oxyethylene) glycol, are most often used in the molding process. The samples obtained with the binders mentioned are characterized by a relatively small density (<63% of theoretical value) and small mechanical strength before and after sintering [1–3].

In order to increase the mechanical strength of the profiles obtained by die pressing, novel water-thinnable polymeric dispersions of an amphiphilic character, i.e. such showing an appropriate ratio of the hydrophilic to hydrophobic parts, were applied [4–6].

Such dispersions should, at their minimal amount, cause a decrease in the friction forces between the ceramic powder particles and between the powder particles and matrix, providing at the same time a high mechanical strength of the green moldings after

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removal of water. The content of organic dispersions should not exceed 0.5–3 mass% with respect to the ceramic powder [7].

The glass transition temperature (T_g) is a very important parameter characterizing polymeric binders. It considerably affects both the rheological properties of powders as well as the basic parameters of ceramic materials obtained with them [8–10]. The determination of the glass transition temperature of polymeric binders, showing the transformation from the glassy state to the highly elastic one, is very important and often indicates the usefulness of a dispersion in the formation of ceramic materials. The T_g determination is most often carried out by the DSC method. This method found broad application in the studies of polymers and simultaneously permits to monitor phase transitions accompanied by slight heat effects, i.e. glass transition temperature, crystallization and polymorphic transformations. Many works have been devoted to this problem [11–17].

The mechanical strength is also affected by the polymer adhesion to the ceramic powder surface and the cohesion of the polymer particles. Many factors have to be taken into account to obtain a good binder for a given process, among others the presence of suitable functional groups in the copolymer to assure good adhesion of the polymer to the ceramic powder. The selection of a monomer mixture composition in the polymer synthesis should be a compromise between obtaining a sufficiently low glass transition temperature of the polymer, its good adhesion to the ceramics and cohesion of the polymer alone.

The purpose of studies was to investigate the effect of the chemical structure of new water-thinnable polymeric binders, obtained with the addition of macromonomers of varied chemical structure, on the properties of samples formed by die pressing and the obtaining of materials of high density (d_w>96%), small open porosity, large mechanical strength (σ_z>300 MPa) and large Weibull modulus (m>10).

Experimental

Materials and sample preparation

Synthesis of polymer dispersions

The water-thinnable binders were obtained by emulsion polymerization and for studies were used in the form of dispersions. These polymeric dispersions are not commercial products and were home made.

The synthesis of water-thinnable polymeric binders has been described earlier [5–6, 18]. The chemical structure of the binders is presented in Table 1.

DSC analysis

The glass transition temperatures were measured by the DSC method in a Perkin Elmer DSC Unipan Pyris 1 microcalorimeter for polymer samples of ~30 mg. DSC condition measurement: hold for 1.0 min at –120°C, heat from –120 to 25°C at 20°C min^{-1}.

Table 1 Chemical structure of polymeric binders

Binder	Chemical structure

PVA[1)]

$$\left[CH_2-CH\right]_n \left[CH_2-CH\right]_m O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$
$$\qquad\qquad OH$$

n:m=7.3:1

AS[2)]

$$\left[CH-CH_2\right]_n \left[CH-CH_2\right]_m$$
phenyl ring ; $O=C$; $O-(CH_2)_3-CH_3$

n:m=1:2.3

VA[3)]

$$\left[CH_2-CH\right]_n \left[CH_2-CH\right]_m$$
O ; CH_2
$O=C-CH_3$; $O-(CH_2CH_2O)_x-CH_3$

n:m=1:1

AA[4)]

$$\left[CH-CH_2\right]_n \left[CH-CH_2\right]_m$$
$O=C$; CH_2
$O-(CH_2)_3-CH_3$; $O-(CH_2CH_2O)_x-CH_3$

n:m=1.5:1

[1)]poly(vinyl alcohol) solution, [2)]poly(acrylic-styrene), [3)]poly(vinyl-allyl), [4)]poly(acrylic-allyl) dispersions

Preparation of ceramic slips

In order to obtain a ceramic casting slip, the solid phase – high purity Al_2O_3 (Martoxid ZS 402/M, Martinswerk, Germany) of density d=3.923 g cm^{-3}, (Al_2O_3 content >99.8%, average grain size 1.5 μm and specific surface measured by the BET

method equal to 6.41 m^2 g^{-1}) was mixed with an aqueous 10 mass% solution of poly(vinyl alcohol) (Mowiol 4-88, Hoechst AG, Germany), water and additives. A casting slip was prepared from aluminum oxide, of the solid phase concentration of 70 mass%, at the 0.25% additive of the dispersing agent with respect to the solid phase, and 0.5 mass% additive of the polymeric binder. After mixing and water evaporation in a laboratory pulverizing drier a white polymer coated ceramic powder was obtained, which was used for die pressing. Casting slips with other polymeric dispersions were prepared analogously.

Forming of samples by die pressing

Cylindrical samples of 20 mm in diameter and ca. 2.5 mm in height were prepared in order to determine the effect of the type of binder on the specific density, open porosity, wettability and strength after sintering as well as the Weibull modulus of samples die pressed. The samples were die pressed on a hydraulic press under the pressure of 50 MPa.

Sintering

The samples obtained were dried in a drier at 105°C for 24 h, and then sintered in a HTC 18/8 furnace of Carbolite (UK) programmed as follows:

heating rate up to 500°C	3°C min^{-1}
heating rate in the 500–1650°C range	5°C min^{-1}
sintering at 1650°C	1 h
cooling rate	5°C min^{-1}

Methods

Studies of physical properties of green samples obtained by die pressing involved the determination of the density and tensile strength by means of the 'Brazilian test', and in the case of sintered samples: open porosity, bending strength by means of the bi-axial tension method (the so-called ball on ring method) and Weibull modulus.

Determination of the tensile strength by the 'Brazilian test' method

In order to determine the mechanical strength of the green samples, from each granulate 10 samples of 20 mm in diameter (ϕ) and 5 mm in height (h_1) were prepared.

The strength of green samples according to the 'Brazilian test' was determined from the relationship:

$$\sigma_r = \frac{2P}{\pi dh} \text{ [MPa]} \tag{1}$$

where σ_r – tensile strength [MPa], P – force causing the destruction of the sample [N], d – diameter of the sample [mm], h – height of the sample [mm].

The rate of the traverse advance, similarly as in the case of bending strength by means of the ball on ring method was 0.02 mm min^{-1}.

Determination of the bending strength by the ball on ring method

The mechanical strength is defined as the ability of a material to stand loads without destruction. It is expressed by means of the magnitude of an external load, at which the material loses cohesion, undergoing separation into two or more parts. The bending strength modulus by the biaxial tension method was calculated from the formula:

$$\sigma_z = \frac{3P(1+v)}{4\pi t^2}\left[1 + 2\ln\frac{a}{b} + \frac{(1-v)}{(1+v)}\left\{1 - \frac{b^2}{2a^2}\right\}\frac{a^2}{R^2}\right][\text{MPa}] \qquad (2)$$

where P – destruction load [N], t – disk thickness [m], a – supporting ring radius [m], b – piston radius [m], R – disk radius [m], v – Poisson's ratio (for a ceramic material v=0.22).

   Samples of diameter ϕ=20 mm and height h_2=2.5 mm were used for the ceramic material strength determination. The 'ball on ring' method is a biaxial bending method, in which a gradually increasing pressure is put on the sample studied.

Determination of the Weibull modulus

The Weibull distribution function describing the probability of destroying an element of a given magnitude, structure surface, microstructure and stress conditions is expressed by the equation:

$$S = 1 - \exp\left[-V\left(\frac{\sigma - \sigma_0}{\sigma_w}\right)^m\right] \qquad (3)$$

where V – unit volume of the material subjected to a load, σ – measured destruction stress, σ_0 – threshold stress, σ_w – normalizing coefficient, m – Weibull modulus.

   The obtained value of the Weibull modulus is connected with the distribution of the mechanical properties, and thus also the microstructure defects [19].

Results and discussion

Four types of binders were selected for studies on the effect of the chemical structure and glass transition temperature in the molding of ceramic powders: poly(acrylic-styrene), poly(vinyl-allyl) and poly(acrylic-allyl) dispersions as well as poly(vinyl alcohol) as the typical water soluble binder used in the forming of ceramic materials. The basic parameters of the binders applied are presented in Table 2.

   As seen from the data presented in Table 2, glass transition temperature is the parameter, which considerably differentiates both groups of binders, and in the case of poly(vinyl-allyl) and poly(acrylic-allyl) ones it is below –50°C, whereas for PVA it is 46°C. Exemplary DSC traces of the acrylic-allyl copolymer is presented in Fig. 1.

   The chemical structure of the polymer has a decisive effect on stiffness, i.e. the possibility of conformational changes of the polymer and thus on the T_g value. In the case of poly(vinyl alcohol) we deal with the main chain of a regular structure and

Table 2 Basic parameters of the applied water-thinnable polymers

Binder	pH[1]	$T_g^{2)}$/°C	$\Delta C_p^{3)}$/J g^{-1} °C^{-1}	$C^{4)}$/mass%	$WA^{5)}$/°	$M_n^{6)}$/g mol^{-1}	$M_w/M_n^{7)}$
PVA	6.0	46.1	–	10.0	70.2	$3.10 \cdot 10^4$	–
AS	4.5	1.8	0.18	32.4	26.1	$6.22 \cdot 10^5$	1.7
VA	1.3	−59.2	0.21	16.7	35.8	$2.36 \cdot 10^4$	5.5
AA	2.4	−55.3	0.22	15.6	37.5	$1.43 \cdot 10^4$	2.5

1) pH of the dispersion or polymer solution, 2) glass transition temperature, 3) specific heat difference of rubbery and glassy states, 4) polymer concentration, 5) wetting angle of aluminum oxide by the polymer dispersion, 6) number average molecular mass, 7) M_w – mass average molecular mass, M_w/M_n – polymer dispersity.
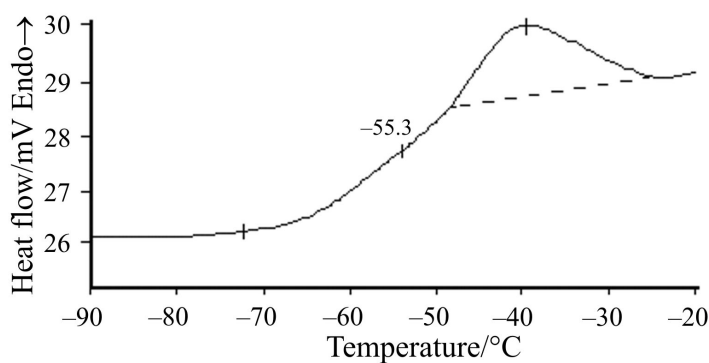

Fig. 1 DSC traces for an acrylic-allyl copolymer

presence of a strong hydrogen bond between the polymer chains. The factors mentioned affected the large T_g value in comparison with other polymers.

Vinyl-allyl and acrylic-allyl copolymers were characterized by the lowest glass transition temperatures, below −50°C. This results from the non-regular structure of the polymer and presence of long and flexible poly(oxyethylene) pendant chains in an amount of 67 and 73 mol%, respectively. These fragments disturb the regular structure pushing away the polymer backbones from each other and thus facilitate the rotation round the backbone C–C bonds.

Simultaneously, the presence of hydrophilic poly(oxyethylene) chains assures a good contact with the Al$_2$O$_3$ grain surface and thus prevents the formation of Al$_2$O$_3$ agglomerates, which in turn limits the friction between grains during die-pressing. This type of relationships is indicated by the results of relative densities of the sinters from 96.3 to 98.4% for water-thinnable copolymers and 93.5% for poly(vinyl alcohol). The acrylic-styrene copolymer was characterized by a glass transition temperature of 1.8°C, which was higher than that of the two other copolymers. Three factors are responsible for this value: lack of groups capable of forming hydrogen bonds, irregular structure of the polymer chain and presence of a phenyl group, which is a 'stiff' group and renders the polymer rotation. The presence of the phenyl group

would affect the relatively high T_g value, if not for the macromonomer L-25 inbuilt in the structure of the amphiphilic polymer.

L25

$$CH_3(CH_2)_n(OCH_2CH_2)_mOCH_2CHCH_2OCCH=CH_2$$

n=15–21   m ~25   OH   O
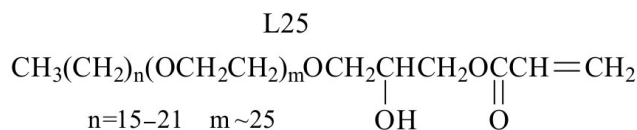
This macromonomer plays the role of an internal plasticizer. However, the share of the macromonomer with a long chain [poly(oxyethylene)] was too small (1.5 mass% with respect to the dispersion) for the glass transition temperature of the acrylic-styrene copolymer to be lower.

The wetting angle is another important parameter of binders. As shown in Table 2, the wetting angle of the poly(vinyl alcohol) solution is about twice as large as that in the case of other binders. The small wetting angle value directly affects the mechanical strength of the green samples (Table 3).

Table 3 Effect of the type of polymeric binder on the density before and after sintering and open porosity of samples from Al_2O_3 formed by die pressing. Binder additive 0.5 mass% with respect to alumina powder

Binder	d_{vo}[1]/%	σ_r[2]/MPa	d_v[3]/%	P_0[4]/%	σ_z[5]/MPa	m[6]
PVA	61.2	0.19±0.05	93.5	5.5±0.3	234±46	5.3
AS	65.0	0.60±0.04	96.3	1.6±0.9	314±30	12.7
VA	63.7	0.26±0.03	98.4	0.5±0.3	509±58	9.3
AA	64.7	0.23±0.06	96.6	2.3±0.1	310±59	7.7

1) relative density before sintering with respect to the density of Al_2O_3 Martoxid ZS 402/M equal to d=3.923 g cm^{-3}, 2) tensile strength of green samples, 3) relative density after sintering, 4) open porosity, 5) bending strength of sintered samples, 6) Weibull modulus.

The wettability of the ceramic powder by the binder decides, among others, of the strength of ceramic materials on the powder–polymer binder interface. Therefore, a very high value of the wetting angle, like in the case of materials based on PVA, is unfavorable. Samples involving PVA were characterized by tensile strength σ_r=0.19 MPa, which was the lowest value of those achieved (Table 3).

Green density is an important parameter for the evaluation of the sample properties before sintering. The larger the green density of the molded samples, the larger their density after sintering. When using water-thinnable copolymers it is possible to obtain large densities of the molded samples. As seen from the data presented in Table 3, samples involving PVA showed the smallest density, both before and after sintering, and the largest open porosity.

The samples involving poly(vinyl-allyl) dispersions can be assumed as non-porous in comparison with others, since the porosity value of <1% is connected with the roughness of the sample surface and lies within the measurement error.

The open porosity of the sintered ceramic samples is the next important feature, which also affects the mechanical strength of ceramic materials. It is characteristic that a large strength of green samples also affects the large strength values after sintering. This is especially clearly visible in the case of samples obtained with the VA binder. The non-porous materials obtained on the basis of poly(vinyl-allyl) dispersions of the largest density were characterized by a very large bending strength, above 509 MPa, over twice as much than that of materials obtained with PVA (σ_z=234 MPa). The results are presented in Table 3.

The Weibull modulus, besides mechanical strength, is another very important parameter characterizing material uniformity. The greater the uniformity of density, the lesser number of defects in the sintered sample microstructure, and thus larger mechanical strength and also larger Weibull modulus. For ceramic materials it lies in the range $5<m<30$ and for samples molded involving PVA it is 5.3, i.e. on the lower threshold. However, the Weibull modulus values, at the binder additive of 0.5 mass% of the polymer with respect to the solid phase, were equal from 7.7 to 12.7 for sinters obtained with water-thinnable copolymers, which confirms the applicability of water-thinnable dispersions containing poly(oxyethylene) pendant fragments for the obtaining of samples by die pressing. The Weibull modulus value of 12.7 is over twice as large as the values obtained for PVA. The large Weibull modulus values indicate a large uniformity of the sinters obtained with poly(acrylic-styrene) binders with a regular distribution of pores and microcracks. The effect of the type of binder on the Weibull modulus of the ceramic materials obtained on the basis of a polymeric binder is presented in Table 3.

Conclusions

It has been shown that polymers characterized by a low glass transition temperature have a distinct effect on the properties of Al_2O_3 ceramic materials obtained by die pressing. The presence of long poly(oxyethylene) side chains in the polymers affect the decrease in the T_g values, and simultaneously increase the polymer adhesion to the Al_2O_3 grains, which causes the obtaining of high density samples.

As far as samples with poly(vinyl alcohol) were characterized by relative density in the green state of 61.2%, strength in the green state of 0.19 MPa, strength after sintering of 234 MPa and Weibull modulus of 5.3, the materials obtained with water-thinnable polymer dispersions showed density of 63.7–65.0%, strength in the green state of 0.23–0.60 MPa, strength after sintering of 310–509 MPa and Weibull modulus of 7.7–12.7.

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