

VINYL ACETATE COPOLYMERS IN DIE PRESSING OF ALUMINA*

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Abstract

The studies on the application of the emulsions of poly(vinyl acetate-co-allyl ether)s containing nonionic hydrophilic poly(oxyethylene) fragments as binders in the die pressing of alumina is presented. It was found that introduction of hydrophilic fragments into molecules of a typical water dispersible polymer led to better polymer affinity to the ceramic powders. It was also shown that low molecular mass of such copolymers should be relatively low ca 1500 g mol^{-1} to increase the density and thickening uniformity of the samples before and after sintering. The resultant sinters indicated exceptionally high mechanical strength (bending strength ca 500 MPa).

Keywords: alumina, die pressing, emulsion of poly(vinyl acetate-co-allyl ether)

Introduction

The type and amount of organic additives used in ceramic processing has a great effect on the properties of the final ceramic product. This concerns especially the bodies obtained from non-plastic starting materials, i.e. such, which contain a small amount of clay minerals or those without clay minerals. In this case polymers of various molecular mass are used to enable formation and sintering of the ceramic products [1, 2].

Water-soluble polymeric binders, such as poly(vinyl alcohol), methyl cellulose, carboxymethyl cellulose and poly(oxyethylene) glycols, are often used in the processing of ceramic powders due to their lower environmental hazard. A disadvantage of this type of binders is the relatively low mechanical strength of green samples obtained. To reduce this flaw, in the recent years, various types of polymers in the form of aqueous emulsions were applied. Poly(vinyl acetate) and polyacrylic emulsions are used most often [3–5]. Special interest is growing in water emulsions of polymers characterized by a large interface surface (above $5 \text{ m}^2 \text{ mL}^{-1}$), as well as high surface functionality [6]. Usually the synthesis of such polymers requires the incorporation of a comonomer with functional groups modifying the structure of the basic polymer chain.

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In this paper the results of studies on the effect of the emulsion of poly(vinyl acetate-co-allyl ether) copolymers containing nonionic hydrophilic poly(oxyethylene) fragments on the properties of alumina processing by die pressing are presented.

Experimental

Materials

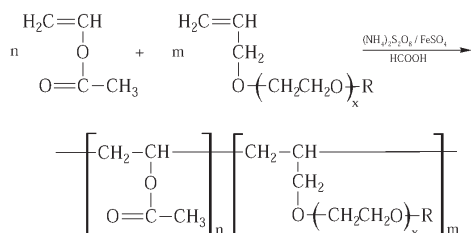
Preparation of the emulsions of poly(vinyl acetate-co-allyl ether)s containing hydrophilic poly(oxyethylene) fragments

The allyl monomers with hydrophilic groups were synthesized according to [7] via Williamson reaction from allyl chloride and commercially available poly(oxyethylene) glycol (350 and 750) monomethyl ethers, butoxyetoxyethanol and tris(oxyethylene) glycol monoalkyl (C₁₀-C₁₄) ether.



where AllTEA – allyltriethylammonium chloride (catalyst).

The emulsion polymerization of 25 g of monomers mixture (allyl ether:vinyl acetate molar ratio 1:9) in 50 g of deionized water was carried out in the presence of ammonium persulphate/Fe(II) salt (0.75 g/0.05 g) redox system at 72–75°C for 4–5 h.



Scheme 1

The commercial emulsion of poly(vinyl acetate) of 35 000 g mol⁻¹ (Chemical Company Dwory SA, Poland) and aqueous solution of poly(vinyl alcohol) of the molecular mass 30 000 g mol⁻¹ (hydrolysis degree 88%) (Merck-Schuchardt, Germany) were also used as polymeric binders.

Alumina

Al₂O₃ ZS 402/M of Martinswerk of average grain size 1.5 μm and specific surface measured by the BET method equal to 6.41 m² g⁻¹ was used for the studies.

Methods

The glass transition temperature (*T*_g) of the binders was determined by DSC method by means of the Pyris 1 apparatus of Perkin Elmer. The molecular mass of the synthe-

sized binders was determined by GPC method on a gel chromatograph LC-10AD of Shimadzu. Thermogravimetric analysis of the binders was carried out using Derivatograph Q-1500 (MOM, Hungary). Microscopic studies of both green and sintered ceramic samples were carried out on a scanning electronic microscope LEO 1530. The mercury porosimetry method (Autopore II 9215 V300 of Micromeritics, USA) for pore diameter measurement was used. The bending strength of the sintered samples was determined using a testing machine Instron 1115 at a rate of crosshead movement of 0.02 mm min^{-1} (ring – bowl). The thickening ability of the ceramic powder containing the binders was determined according to the modified method elaborated by Mironiec *et al.* [8]. It consists in the determination of the average pressure P_a necessary to press in the same matrix profiles of identical apparent density but of two different heights (5 and 15 mm). The smaller is the P_a value, the greater is the thickening ability of the granulated product.

Preparation of the granulated product, molding of ceramic samples and their sintering

Casting slips were prepared from alumina of solid phase concentration of 70 mass% with the addition of a deflocculant (ammonium salt of poly(acrylic acid) – Dispex A-40 of Applied Colloids) (0.25 mass% in respect to the solid phase) and the polymeric binder (0.5 mass%). The granulated product was obtained from the thus prepared casting slip and the fraction of 0.2–0.5 mm grain diameter was applied for further studies.

In order to determine the effect of the binder on the apparent density, open porosity, mechanical strength after sintering and Weibull modulus, cylindrical profiles of 20 mm in diameter and ca 2.5 mm in height were prepared. The samples were uniaxially pressed (pressure 50 MPa) on a hydraulic press.

The green ceramic samples were dried at 105°C for 24 h, and then sintered in a furnace type HTC 18/8 of Carbolite, UK; heating rate up to 500°C : 3°C min^{-1} , heating rate in the $500\text{--}1650^\circ\text{C}$ range: 5°C min^{-1} ; heating at 1650°C : 1 h; cooling rate: 5°C min^{-1} .

Results and discussion

The emulsions of poly(vinyl acetate-co-allyl ether)s (VA-1-VA-4) containing different length of hydrophilic poly(oxyethylene) fragments were chosen for the studies on the application of the polymeric binders in the die pressing of ceramic powders. For comparison the emulsion of the unmodified poly(vinyl acetate) (PVAc) and water-soluble poly(vinyl alcohol) (PVA) were also used.

Due to autoinhibition of allylic monomers (degradative chain transfer) the molecular mass of the copolymers with vinyl acetate obtained by emulsion polymerization was rather low and did not exceed 1600 Da. Allyl ethers with different hydrophilic fragments: bis(oxyethylene) with butoxy end group (VA-1, Table 1), poly(oxyethylene) 240 ended with long aliphatic chain ($\text{R}=\text{C}_{10}\text{--}\text{C}_{14}$) (VA-2) and poly(oxy-

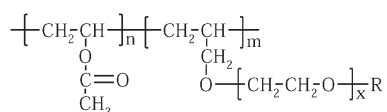
ethylene) 350 with methoxy end group (VA-3) were used as comonomers. The amount of the allyl monomer in the copolymers was in the range 24–34 mass%. However, when allylmethyl ether of poly(oxyethylene) glycol 750 monomethyl ether (the monomer with longer poly(oxyethylene) chain) was used as the comonomer in the emulsion copolymerization with vinyl acetate the final product of molecular mass of ca 35 000 g mol⁻¹ was obtained (VA-4). The characteristics of these binders as well as PVAc and PVA are presented in Table 1.

Table 1 Characteristics of binders applied in the uniaxial pressing of alumina

Binder	$T_g/^\circ\text{C}$	Mass loss in air ^a /mass%		Chemical structure of the binder ^b	Molecular mass/g mol ⁻¹
		450°C	700°C		
VA-1	-30.1	85.1	96.0	$x=2, R=\text{C}_4\text{H}_9, n/m=5\div 7$	1450
VA-2	-35.7	85.3	95.9	$x=3, R=\text{C}_{10}-\text{C}_{14}, n/m=6\div 8$	1500
VA-3	-59.2	84.2	95.8	$x=7, R=\text{CH}_3, n/m=6\div 8$	1570
VA-4	-50.7	83.1	97.8	$x=16, R=\text{CH}_3, n/m=11\div 13$	35800
PVAc	28.6	82.7	92.5	$m=0$	35000
PVA	46.1	82.0	91.8	$-(\text{CH}_2-\text{CH}(\text{OH}))_n-$	30000

^aThermogravimetric analysis – heating rate 10°C min⁻¹

^b



The introduction of the monomer with pendant poly(oxyethylene) group led to the reduction of the glass transition temperature of poly(vinyl acetate) from 28.6 to the value lower than -30°C. From the DTG-curves it was found that thermal degradation of such copolymers proceeds in a three-step mode with maxima at 220, 320 and 410°C. At 700°C the decomposition degree of the binders of low molecular mass was higher than 90%.

The effect of the polymeric binders on the thickening ability of alumina powders during die pressing and other properties of the molded samples before and after sintering are presented in Table 2.

The presence of the hydrophilic allyl ether monomers in the poly(vinyl acetate) macromolecules caused an increase in the wettability of the ceramic powders, which led to a more uniform covering of the ceramic powder with the binder applied and increase in ability of alumina powder to press molding. The highest thickening was observed for binders of rather low molecular mass, marked VA-1-VA-3, containing poly(oxyethylene) fragments as pendant groups. It was found that the thickening did not depend on the end group of the hydrophilic fragments.

Table 2 Effect of the polymeric binders on the properties of the molded samples with Al₂O₃ formed by uniaxial pressing (pressing pressure 50 MPa; sintered at 1650°C for 1 h)

Binder ^a	P_h^b / MPa	P_{3h}^c / MPa	P_a^d / MPa	d_w^e	P_o^f / %	δ_{zg}^g / MPa	Weibull modulus ^h
VA-1	76±4	29±3	64.2	0.981	0.59	515±47	8.6
VA-2	36±3	18±2	31.5	0.979	0.90	534±65	12.9
VA-3	99±6	58±5	88.7	0.984	0.52	509±58	9.3
VA-4	90±3	36±3	76.5	0.969	2.20	304±34	10.3
PVAc	74±4	32±2	63.5	0.946	4.90	269±38	5.6
PVA	63±2	41±3	57.5	0.955	4.05	234±46	5.3

^aChemical structures of the poly(vinyl acetate-allyl ether) binders are presented in Table 1

^bPressure necessary to obtain a ceramic sample of 5 mm in height and 2.7 g cm⁻³ in density

^cPressure necessary to obtain a ceramic sample of 15 mm in height and 2.7 g cm⁻³ in density

^dAverage pressure of press molding of ceramic samples of 2.7 g cm⁻³ density

$$P_a = \frac{P_{3h} + 3P_h}{4}$$

^eApparent density of samples after sintering at 1650°C for 1 h

^fOpen porosity of samples after sintering at 1650°C for 1 h

^gBending strength of samples after sintering at 1650°C for 1 h

^hWeibull modulus of samples after sintering at 1650°C for 1 h

The apparent density is one of the most often applied parameters for the evaluation of the properties of sintered bodies. The greater the apparent density of the pressed samples before sintering is, the greater their density after sintering is. The greatest density values for the pressed samples were achieved when poly(vinyl acetate-co-allyl ether)s of low molecular mass were used as binders (Table 2).

It is worth underlining that the mechanical strength of the pressed and sintered alumina samples prepared using poly(vinyl acetate-co-allyl ether)s (VA-1-VA-3) were unexpectedly high (bending strength ca 500 MPa), almost 70% higher than the one when higher molecular mass poly(vinyl acetate-co-allyl ether) (VA-4), as well as PVAc and PVA, were applied.

Weibull modulus of ceramic samples obtained using vinyl acetate – allyl ether copolymers was also higher (8.6–12.9) than the one when water soluble PVA or water thinnable PVAc (ca 6) were applied. Such high values of Weibull modulus indicate that samples prepared using amphiphilic copolymers are characterized by greater uniformity of density and fewer defects in the microstructure of the sintered sample are present.

Also the smallest open porosity (0.5–0.9%) of sinters was observed for ceramic samples prepared using this kind of modified polymeric binders (Table 2). SEM pictures of the fractures of the ceramic samples obtained involving poly(vinyl acetate-co-allyl ether)s, presented in Fig. 1, confirmed that the structure of the sinters were very uniform, while those obtained involving PVAc (Fig. 2) had some amount of bigger pores besides small ones.

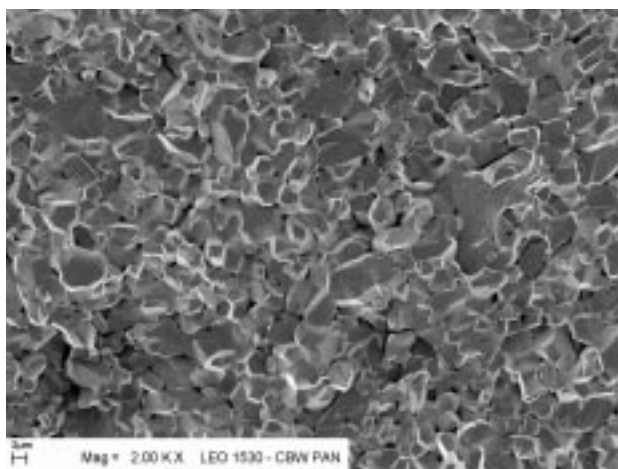


Fig. 1 The SEM picture of the fracture of the alumina powder molded by die pressing and sintered at 1650°C using the poly(vinyl acetate-co-allyl ether) (VA-3) binder

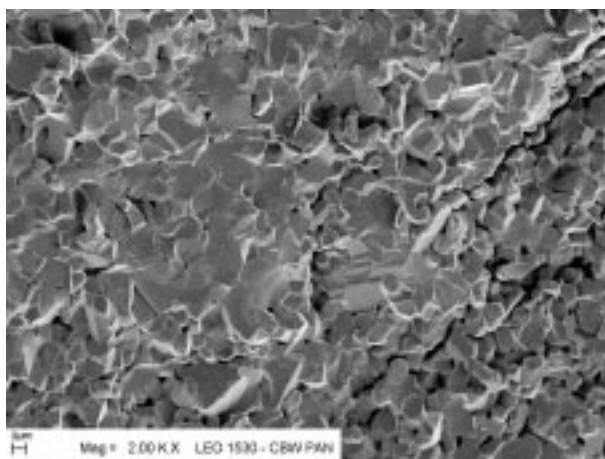


Fig. 2 The SEM picture of the fracture of the alumina powder molded by die pressing and sintered at 1650°C using the poly(vinyl acetate) (PVAc) binder

Thus, the good wettability of the ceramic grains was achieved by the introduction of the nonionic hydrophilic poly(oxyethylene) fragments into poly(vinyl acetate) macromolecules. Additionally to reduce the viscosity resistance during the ceramic powders processing the molecular mass of such amphiphilic copolymers should be in the range of 1500–2000 g mol⁻¹. These relatively short polymer chains played a role of a lubricant during the ceramic powder die pressing. Moreover, the important factor, which makes the polymeric binder flexible at room temperature, is its low glass transition temperature ($T_g < -30^\circ\text{C}$).

Conclusions

The studies on the application of the poly(vinyl acetate) emulsions as binders in the die pressing of alumina by the uniaxial pressing method showed that the introduction of non-ionic hydrophilic poly(oxyethylene) fragments to molecules of a typical water dispersible polymer led to better polymer affinity to the ceramic powders. It was also shown that low molecular mass of such copolymers (ca 1500 g mol⁻¹) is optimal for the thickening of the ceramic powders leading to the increase in density and thickening uniformity of the samples before and after sintering, and also to exceptionally high mechanical strength of the ceramic sinters.

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