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Short communication

Effect of polymer concentration on porosity and pore size characteristics of alumina membrane substrates prepared by gelcasting

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Abstract

The effect of urea–formaldehyde (UF) polymer concentration on porosity and average pore size of alumina membrane substrates prepared by gelcasting has been studied. The soluble UF oligomers formed in the initial stages of polymerization act as steric stabilizer for alumina particles in the suspension. The porosity and average pore size of the substrate samples decreased with both the decrease of amount of polymer in the gelcast body and the increase of sintering temperature. Membrane substrates obtained by sintering of gelcast bodies containing UF polymer concentrations from 24.3 to 15.6 wt% at temperatures from 1250 to 1450 °C showed porosity and average pore size of 62.5–27 vol% and 0.43–0.20 μm, respectively. The membrane substrates prepared by the gelcasting method had narrow pore size distribution.

Keywords: A. Suspension; B. Porosity; D. Al_2O_3; E. Substrates; Gelcasting; Urea–formaldehyde

1. Introduction

Recently, the gelcasting process has been used for preparation of porous alumina substrates for ceramic membranes that find application in biotechnology, treatment of waste and drinking waters, pharmaceutical industry, nuclear industry and desalination of seawater for making it suitable for drinking by reverse osmosis [1–4]. The authors have reported a urea–formaldehyde (UF) gelcasting process for the fabrication of microporous alumina membrane substrate of high porosity [5]. In this process, the urea–formaldehyde polymer used in excess as gelling agent acts as template for pores. By this method we could achieve a porosity of more than 70% from slurry of alumina loading 23 vol% (UF polymer concentration 26.5 wt%). However, the average pore size of the substrate samples sintered at temperature from 1250 to 1450 °C is in the range of 0.48–0.56 μm. The substrates prepared by this method as such would be useful for separation of microbes from drinking water. It is expected that membrane substrates with lower average pore size could be prepared by decreasing the polymer concentration (increasing the alumina loading in the suspension). In the present work, the effect of UF polymer concentration on porosity and pore size of microporous alumina substrates prepared by gelcasting is reported.

2. Experimental

An alumina powder (A16SG, ACC Alcoa India) of average particle size 0.34 μm and surface area 10.4 m^2/g and analytical reagent grade urea and formaldehyde solution (37%, w/v) (S.D. fine chemicals, India) were used. Analytical reagent grade dilute HNO_3 (Merck, India) and NaOH (Merck, India) solution were used for pH adjustments. Methylol urea solution was prepared by dissolving 1 mol urea in 4 mol formaldehyde solution adjusted to a pH of 8.5 and aging for 24 h [5].

The preparation process of microporous alumina substrates by gelcasting is reported elsewhere [5]. Slurries of alumina loading in the range of 28–42.5 vol% were prepared by 6 h ball milling the alumina powder in methylol urea solution at pH 2 using zirconia grinding media. The slurries were supplemented with additional urea to make the mole ratio of urea and formaldehyde 1:2 and then cast in the form of circular disc of diameter 30 mm and thickness 10 mm in an open glass mold. After gelation, the slurries were removed from the mold and dried at 75% relative humidity at 30 °C. Polymer removal from the dried gelcast samples was carried out by heating at a rate of

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5 °C/h up to 300 °C and then 60 °C/h up to 600 °C. After binder removal, the substrate samples were sintered at various temperatures from 1250 to 1550 °C for 2 h with a heating rate of 300 °C/h up to the sintering temperature.

The viscosity of the slurries was measured using a Brook field viscometer (RVT Model) using a small sample adapter and a cylindrical spindle (SC-21). The yield stress value of the slurries was calculated using the Casson model [6]. The polymer content in the dried gelcast sample was estimated by thermo gravimetric analysis (Hi Res TGA 2950, TA Instruments). Porosity, average pore size and pore size distribution of the substrate samples were measured using a mercury porosimeter (Thermo Finnigan, Pascal 440). Microstructure of fractured surface of the membrane substrate samples was observed by a Scanning Electron Microscopy (LEO 1455).

3. Results and discussion

The alumina powder disperses in methylol urea solution at pH 2 by electrostatic mechanism due to protonation of surface hydroxyl groups [6]. The suspensions with alumina loading in the range of 28–42.5 vol% showed viscosity (at shear rate of 4.65 s^{-1}) and yield stress values in the ranges of 0.2–2.2 Pa s and 0.36–9.12 Pa, respectively. Up on the addition of urea, viscosity and yield stress of the suspensions decreased from 0.1 to 0.5 Pa s and from 0.16 to 1.85 Pa, respectively. It appears that the soluble UF oligomers formed in the initial stages of reaction between methylol urea and urea act as dispersant for alumina through a steric mechanism. The decrease in viscosity and yield stress is attributed to better dispersion of the powder by a combination of electrostatic and steric mechanisms. Fig. 1 shows viscosity versus shear rate plots of suspensions of various alumina loading before and after urea addition.

The slurries cast in moulds set in to strong gels within 10 min. The amount of UF polymer present in the gelcast green bodies prepared from slurries of alumina loading from 28 to 42.5 vol% is in the range of 24.3 to 15.6 wt%, respectively (Table 1). Fig. 2A and B shows porosity and average pore size of the alumina membrane substrate samples obtained by sintering of gelcast bodies containing UF polymer concentration from 24.3 to 15.6 wt% at sintering temperatures from 1250 to 1450 °C. The porosity and average pore size of the membrane substrates decreased with the decrease in UF polymer concentration in the gelcast bodies. At a particular UF polymer concentration, the porosity and average pore size of the substrates decreased with the increase in sintering temperature. Membrane substrates with porosity and average pore size in the ranges of 62.5–27 vol% and 0.43–0.20 μm, respectively could be prepared by sintering gelcast alumina bodies containing UF polymer concentration from 24.3 to 15.6 wt% at temperatures of 1250–1450 °C.

Table 1
Amount of UF polymer present in gelcast alumina samples prepared from slurries of various alumina loading.

Slurry loading (vol%)	Polymer content in the green body (wt%)
28	24.3
33	20.7
38	17.5
42.5	15.6

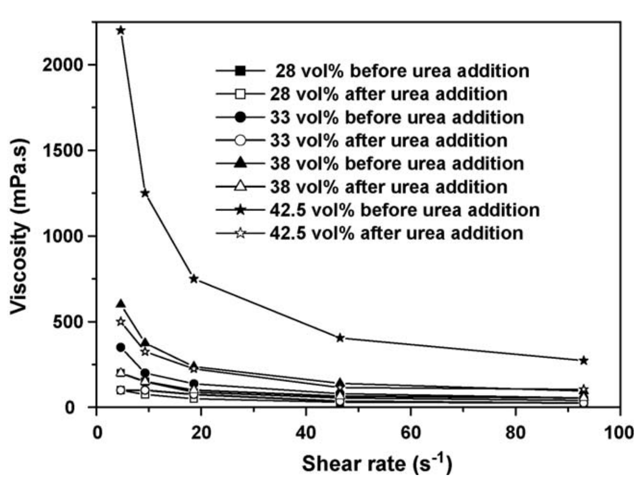

Fig. 1. Viscosity at various shear rates of gelcasting slurries of different alumina loading before and after the addition of urea.

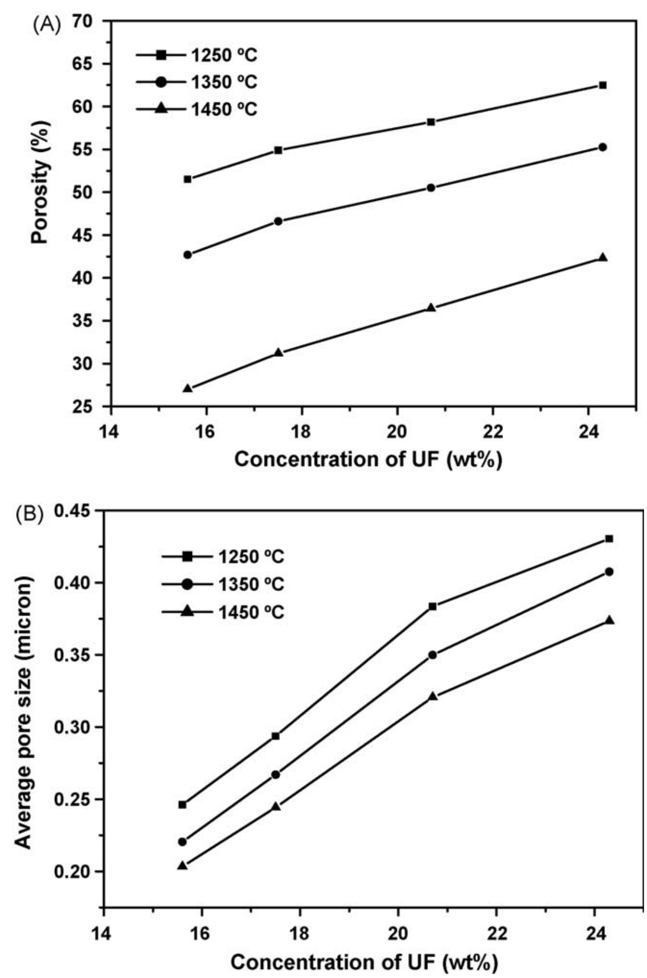

Fig. 2. Porosity (A) and average pore size (B) of the membrane substrates versus concentration of UF polymer in the gelcast body.

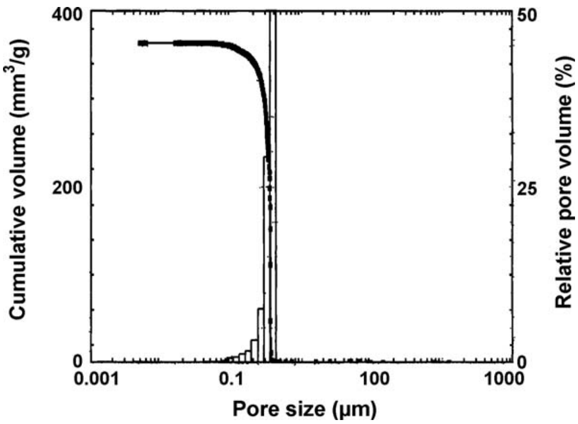

Fig. 3. Pore size distribution of membrane substrate sample prepared by sintering of gelcast alumina body containing 20.7 wt% UF polymer at 1250 °C.

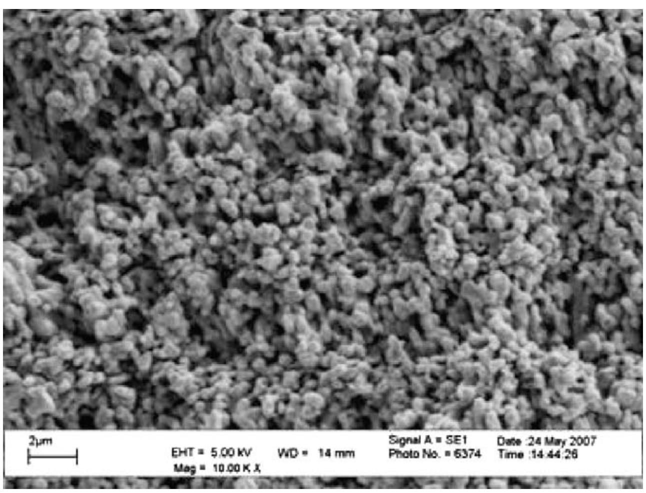

Fig. 4. SEM microstructure of fractured surface of the membrane substrates prepared by sintering of gelcast body containing 20.7 wt% UF polymer at 1450 °C.

The membrane substrate samples prepared from gelcast green bodies containing UF polymer concentration from 24.3 to 15.6 wt% in general showed narrow pore size distribution. Fig. 3 shows typical pore size distribution of membrane substrate sample prepared by sintering gelcast alumina body containing UF polymer concentration of 20.7 wt% at 1250 °C. In this, about 95% of the pore size ranges from 0.20 to 0.43 μm. Out of this nearly 55% of pore size is in the narrow range of 0.43–0.35 μm. It is observed that lowering the amount of UF polymer in the gelcast body and increasing the sintering temperature results in membrane substrates with more narrow pore size distribution. Microstructure studies show the gelcast body after polymer burnout contains loosely packed alumina particles. However, well-defined pores are observed in microstructure of substrates sintered at temperature from 1250 to 1450 °C. Fig. 4 shows a SEM micrograph of a fractured surface of a membrane substrate prepared by sintering a gelcast sample containing 20.7 wt% UF at 1450 °C.

4. Conclusions

The urea–formaldehyde oligomers formed in the initial stages of polymerization act as steric stabilizer. The amount of UF polymer present in the gelcast alumina controls the porosity and pore size such that porosity and average pore size of the membrane substrates decreased with decrease of UF polymer concentration in the gelcast body. Alumina membrane substrates with average pore size from 0.43 to 0.20 μm and porosity from 62.5 to 27% could be prepared by sintering of gelcast alumina green bodies containing UF polymer concentrations 24.3–15.6 wt% at temperature of 1250–1450 °C.

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