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Flexible polyurethane foams as templates for cellular glass–ceramics

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ABSTRACT

In this work flexible polyurethane (PU) foams were obtained with varying air permeability, cell diameter and morphology. The addition of up to 1.5 g anti-foamer with a mixing time of 75 s resulted in larger cell diameters, higher air permeability and lower distorted area. PU foams obtained were used as templates to produce glass–ceramic (GC) foams by the replication method. Glass powder of the LZSA (Li_2O–ZrO_2–SiO_2–Al_2O_3) system was used to infiltrate the PU foams. The retention capacity of the ceramic suspension in PU foam is increased with a reduction of the cell diameter. In contrast, the infiltration capacity increases with raise of the cell diameter. The permeability reduction of GC foams with respect to PU foams varied from 3% to 25% when 2.7 and 0.8.0 mm cell diameters were used, respectively. The results of mechanical characterization were coherent with the morphological characteristics in both PU and GC foams.

1. Introduction

Cellular ceramic structures obtained from polymeric foam templates present high porosity, low density, high chemical stability, structural uniformity, and high surface area. These properties make these structures interesting for a variety of applications such as filters, catalyst supports, membranes, thermal insulators, among others (Gibson and Ashby, 1997; Scheffler and Colombo, 2005).

The performances of cellular ceramic structures depend on cell morphology and on material composition. This leads to the conception of several fabrication technologies according to the application. The polymeric sponge method, also known as replication method, offers a simple, inexpensive and versatile way for producing ceramic foams. This method consists of dipping the polymeric sponge into a slurry containing ceramic particles and appropriate additives (binders and dispersants) followed by drying to evaporate the solvent, heating to burn out the organic part, and sintering to form an open-cell ceramic skeleton (Schwartzwalder and Somers, 1963). The final product is a ceramic with the initial form of the polymeric foam but with a volumetric shrinkage or expansion. The most common applications for open-cell ceramics are as supports for catalysts, and filters for molten metal and hot exhaust gases (Studart et al., 2006).

Glass–ceramic (GC) materials have found applications in many fields thanks to important properties such as low coefficient of thermal expansion, high abrasion and scratch resistance, and good chemical and thermal shock resistance. Due to their unique characteristics, glasses belonging to the Li_2O–ZrO_2–SiO_2–Al_2O_3 (LZSA) have been used in powder technology processing by various forming methods such as extrusion (Montedo et al., 2004; Bertan et al., 2009), injection molding (Giassi et al., 2005), tape casting (Gomes et al., 2006), and rapid prototyping (Gomes et al., 2008).

Particularly, the production of cellular glass–ceramics constitutes a new class of processing technology, which has been in recent times successfully explored (Sousa et al., 2005; Rambo et al., 2006). A critical variable for the fabrication process corresponds to the polymeric foam morphology (Silveira et al., 2007). The infiltration capacity of the ceramic suspension into the foam, the retention of the slurry, and the final characteristics of the ceramic structure depend directly on the polymeric foam cell diameter and distribution (Zhu et al., 2001; Sarmiento, 2006; Sousa et al., 2008).

This paper deals with preparing and modifying the morphology of a polyurethane flexible foam, used as template in a parent glass suspension for the fabrication of cellular glass–ceramics, and evaluating the performance of the final cellular structures.

2. Experimental procedure

2.1. Raw materials for PU foam

The formulation used for the foam preparation is shown in Table 1. The amounts of polyether polyol, water, silicone surfactant, amine and tin catalysts, and isocyanate were held constant, whereas the amount of anti-foamer was varied according to a fac-

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Table 1
Formulation used for the flexible polyurethane foam.

Material	Parts per hundred polyol (pphp)	Amount
Poliol Polyether polyol initiated with glycerine OH number: 56 Theoretical functionality: 3 Producer: Dow	100	900 g
Water	2.50	22.50 g
Silicon surfactant Non-ionic, silicone-based Proprietary composition Producer: Goldschmidt	0.80	7.20 g
Amine catalyst 33% triethylene diamine in dipropylene glycol 70% bis(dimethylaminoethyl)ether 30% dipropylene glycol Producer: Air Products	0.15	1.35 g
Tin catalyst Stannous octoate Producer: Air Products	–	1.0 ml
Isocyanate TDI 80 Toluene diisocyanate 80/20 mixture of the 2,4 and 2,6 isomers Producer: Dow	–	340.20 g
Anti-foaming agent Linear chain of polydimethylsiloxanes Proprietary composition Producer: Goldschmidt	–	Variable

torial design, as explained in the next section. These raw materials were mixed in three different stages: first, polyol, silicone surfactant, amine catalyst and water; second, this blend with tin catalyst, and last, the whole polyol mixture with isocyanate.

2.2. Experimental design for PU foam

A factorial design was applied, taking into account the possibility of modifying and controlling the morphology of the flexible polyurethane foam template for the production of porous ceramics. The experimental design established two factors to be analyzed: amount of anti-foaming agent (4 levels), and mixing time (3 levels). The latest factor makes reference to the first of the three mixing stages of a typical PU flexible foam fabrication process. Table 2 shows the factors and the levels selected.

2.3. Characterization of PU foams

The response variables were air permeability, cell diameter, and distortion area. The cell diameter and permeability measurements were made according to ASTM D3576 (2004), and ASTM D3574 (2005), respectively, using a flowmeter (Uehling, model ZK, USA).

Table 2
Factors and levels of the experimental design for PU foams.

Factor	Levels
Content of anti-foaming agent (g)	0.7 0.9 1.1 1.3
Mixing time (s)	15 45 75

Table 3
Composition of the parent glass suspension.

Component	Quantity (g)
Parent glass	100.0
Bentonite	5.94
Water	100.63
Sodium silicate	1.07

The air permeability was calculated based on the Forchheimer equation, described as:

$$\frac{\Delta P}{L} = \frac{\mu}{k_1} V + \frac{\rho}{k_2} V^2 \quad (1)$$

where ΔP is the pressure drop; L, the medium thickness; μ and ρ, the viscosity and density of the fluid, respectively; and V, the volumetric flow rate per unit of cross section area. The parameters k_1 and k_2, correspond to the Darcyan and non-Darcyan permeability parameters, respectively. Both constants depend exclusively on the medium characteristics (Moreira et al., 2004).

The first term of Eq. (1) may be attributed to laminar flow; the second, to turbulent flow. In this case, only laminar flow was considered, since $Re < 2000$ was applied to the experimental measurements (Mills, 2005). Hence, the permeability can be determined using Eq. (2):

$$k_1 = \frac{\mu \cdot V}{\Delta P / L} \quad (2)$$

The distorted area of foams was quantified from digital images with the help of the software Image J (Rasband, 2008). A picture of the superficial area of the inferior view of a 380 mm × 380 mm × 200 mm foam sample was taken. A percentage of occupied area was quantified by the cells with smallest cell diameter over the whole surface. An optical microscope (Metallux II, Leitz, Germany) was used.

In addition to the morphological foam evaluation, a mechanical characterization of the foams was made with selected PU foams in a universal testing machine (Instron, Model 4202, USA) according to ASTM D3574 (2005), which involves standard methods for conditioning of foam samples and for testing the basic physical properties: density, tensile strength, tear resistance, airflow, resilience, indentation force deflection, compression force deflection and constant deflection compression set.

2.4. Raw materials for GC foams

LZSA glass with nominal composition of $11.7Li_2O–12.6ZrO_2–68.6SiO_2–7.1Al_2O_3$ was prepared from Li_2CO_3, $ZrSiO_4$ and SiO_2 and $LiAlSi_2O_6$ (spodumene) as raw materials. The template powders were placed in a mullite crucible and melted at 1500 °C for 2 h in a gas furnace. The melt was quenched in water, dried and subsequently milled.

The formulation of the ceramic suspension was composed of a liquid phase (water and sodium silicate, used as a dispersant) and a solid phase (glass powder of LZSA, $Li_2O–ZrO_2–SiO_2–Al_2O_3$, and bentonite, used as a binder). A detailed study on formulation of the parent glass suspension according to rheological measurements can be found elsewhere (Rambo et al., 2006). Bentonite presents as main chemical components SiO_2 (62.8 wt%), Al_2O_3, (20.3 wt%), Fe_2O_3, (3.8 wt%), Na_2O (2.4 wt%), MgO (2.3 wt%) and CaO (1.2 wt%), corresponding to montmorillonite as a main phase and quartz as an impurity (Bertan et al., 2009).

According to an optimized composition, Table 3, the slurry was prepared with 48.5 wt% water, containing 48.2 wt% parent glass powder (LZSA), 2.9 wt% bentonite (Colorminas, Brazil), used as a binder, and 0.5 wt% sodium silicate (Merck, Natronwasserglas