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Preparation of a reticulated ceramic using vegetal sponge as templating

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Abstract

This paper describes the preparation of a reticulated ceramic that combines the morphology of vegetal sponge with ceramic properties, such as thermal stability, resistance to chemical attack, elevated porous degree and reticulation. In this method sponge samples are dipped into a colloidal suspension of 50% clay, 35% feldspar and 15% sand (w/w), followed by drying and heat treatment at 1175 °C for 120 min. Thermogravimetric analysis (TGA) of the vegetal sponge showed that the organic material is completely eliminated at temperatures around 515 °C. X-ray diffraction (XRD) analysis of the reticulated ceramic indicated the presence of mullite and cordierite. Scanning electron microscopy (SEM) of the reticulated ceramic showed the presence of two groups of porous ceramics, one in the range of 5–10 μm which was formed along the wall of the filaments, and another formed as a negative structure of the sponge filaments, measuring approximately 300 μm of diameter.

Keywords: *Luffa cylindrica*; Sponge; Reticulate ceramic; Biomimetic; Template

1. Introduction

Sponge gourd, *Luffa cylindrica* (L.) (Cucurbitaceae) is a tendril-bearing herb in which male flowers occur in raceme clusters while female flowers are solitary [1]. The density of the dry sponge gourd is very low and is constituted of fibers designed in a tri-dimensional network, thus enabling it to be used as catalyst support, enzyme immobilization, etc. [2]. Generally, plant fibers are mainly composed of cellulose, hemicellulose and lignin [3]. The mechanical properties of plant fibers are conferred by cellulose fibers, which are enclosed by the other two main components: hemicellulose and lignin [4,5]. Cellulose can be found as intertwined microfibers in the cell wall, whose size is related to plant specie and is composed of a partial crystalline phase where the cellulose chains are tied through hydrogen bonds [6]. The natural cellulose is a linear macromolecule formed by b–d anhydroglucose units linked together by 1.4-glucosidic bonds [7–9]. Hemicellulose is composed of different types of cycled saccharides such as xylose, mannose and glucose, among others. It forms a highly branched random structure and is mainly amorphous [10]. Lignins are amorphous polymers consisting of phenyl-propane units, mainly comprised of aromatic units such as guaiacyl, syringyl and phenylpropane [6].

Reticulated ceramics are materials made up of interconnected voids surrounded by a ceramic net, perceived to have high permeability and low density [11], thus rendering them suitable for many applications [11]. These include filters, catalysts, sensors, implants, among others [12]. The degree of reticulation and the final properties depend on the manufacturing method and on the starting ceramic material [13]. Reticulated ceramic with reticulation degree on the millimeter scale is usually made from the polymeric foam method. The main demerit of this method is the accumulation of ceramic powders on the peripheral part of the sponge, which leaves to formation of a non-homogeneous reticulated ceramic. To avoid this problem rigorous control of the tixotropy and the homogeneity of the slurry are necessary [14,15].

The objective of this work is to prepare and characterize reticulated ceramic containing a degree of reticulation in the millimeter scale, ranging from 5 to 10 mm, using vegetal sponge, originated from the *L. cylindrica* specie, as template. X-ray diffraction (XRD) analysis of powdered fibers of reticulated ceramic showed this material to be made up of cordierite and mullite.

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2. Experimental

A transversal section of 30 mm of thickness was cut from the internal part of the vegetal sponge originating from the *L. cylindrica* specie. It was then submitted to ultrasound bath for 15 min in distillated water, to remove residues from the sponge filaments. Afterwards, the sponge samples were immersed in acetone and dried in an oven at 50 °C for 10 min. Samples prepared with this procedure were named CF-50.

The ceramic slurry was prepared by mixing 50% (w/w) clay (São Simão, Brazil), 35% (w/w) feldspar (Mil Minérios, Brazil) and 15% (w/w) sand (Jundu, Brazil) in a convenient volume of distillated water to obtain slurry with a specific weight of 1.90 g/cm^3 and four drops of the dispersing agent ammonium polyacrylate (Disperlam). The homogenization of the slurry was performed in a ball milling at ambient temperature for 60 min.

The cleaned sponge samples were then immersed in the slurry, removed after 2 min and dried in an oven at 50 °C for 20 min. The immersion procedure was repeated again and the sample was dried in the same temperature for 60 min. This sample was named as IF-60.

Compact bars were used to evaluate the temperature and time for sintering the reticulated ceramic. These conditions were determined from shrinkage behavior analysis of the compact bars under thermal treatment. The bars were prepared using the ceramic slurry previously described. Initially, the bars (53.3 mm × 5.6 mm × 4.1 mm) were pressed uniaxially (40 MPa, Carver prense), isostatically (300 MPa, Paul Weber prense, KIP 100E) and dynamically heated, in an EDG—EDGCON 1700 equipment, at 10 °C/min from room temperature to: 1000, 1050, 1100, 1150, 1200, 1250, 1300, 1350 and 1400 °C. Immediately after reaching each temperature, the bars were removed from the furnace. After regaining room temperature, their lengths were measured. Once the best sintering temperature was determined (1175 °C), some bars were calcined at 1175 °C for several times: 4, 15, 30, 60, 90 and 120 min. Calcination at 1175 °C for 120 min was the best sintering condition for the compact bars.

A sample of cleaned vegetal sponge (CF-50) was analyzed by thermal gravimetric analysis (TGA) in a Dupont 2100 Thermal Analysis equipment, under atmospheric air at a heating rate of 10 °C/min. XRD patterns of sintered samples were obtained in a Philips PW 1050 and PW 1830 with filtered Cu Kα radiation equipment. The microstructure of the sintered reticulated ceramic was investigated using a scanning electron microscope (SEM, DSM 950 ZEISS). Apparent density or bulk density of reticulated ceramic was measured using the Archimedes method.

3. Results and discussion

Fig. 1 shows the thermogravimetric analyses of the *L. cylindrica* vegetal sponge. Fig. 1 shows that thermal decomposition of *L. cylindrica* takes place in three consecutive stages. The first step, from 25 to 100 °C, is normally attributed to elimination of adsorbed water. Lojewska et al. [16] observed that adsorbed water in the cellulose molecules is very difficult to extract due to the cellulose–water interaction, as observed by computational simulation of cellulose–water molecules [6]. The second one, from 190 to 330 °C, can be attributed to hemicellulose decomposition and the third one (330–515 °C) refers to cellulose pyrolization. It has been observed that hemicellulose decomposition occurs from 220 to 315 °C and cellulose decomposition occurs between 315 and 400 °C [6]. After this temperature the cellulose was completely pyrolyzed and solid residuals were about 7 wt% [6]. The kinetic of cellulose pyrolysis has been extensively investigated by numerous researchers and many kinetic schemes have been proposed. However, despite the research efforts, the mechanisms of cellulose pyrolization are not fully known [17–21]. The third main component of natural fiber is lignin, and its decomposition occurs in a high temperature range, starting below 200 °C and rising to 700 °C [6]. After 515 °C the residual mass is constant, indicating all organic compounds were converted to carbon dioxide. The little residual mass is related to oxides of the inorganic substances present in the original composition of the vegetal fibers. It is important to consider that 515 °C is the lowest temperature to be used in the sintering step, since all organics are removed only after this temperature.

Fig. 2 shows the dependence of linear shrinkage of the compact bar with temperature. This figure shows that linear shrinkage values increased in the range from 1000 to 1250 °C and after 1250 °C its values decreased. It is known that the system $K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$, mullite and silica are formed during the calcination of these starting materials. Analysis on the phase diagram in the region constituted by these materials shows the presence of an invariance point at 980 °C, related to the formation of silica liquid phase [22,23]. A tiny increasing in linear shrinkage is observed in the temperature range of 1000–1100 °C and an abrupt increasing occur in linear shrinkage values after 1100 °C. These behaviors are related to a fraction of the ceramic particle that is wetted by silica liquid, which is related to the viscosity values of the liquid phases [24]. When the viscosity of the liquid phase is very elevated, below 1100 °C, the liquid does not spread efficiently over the

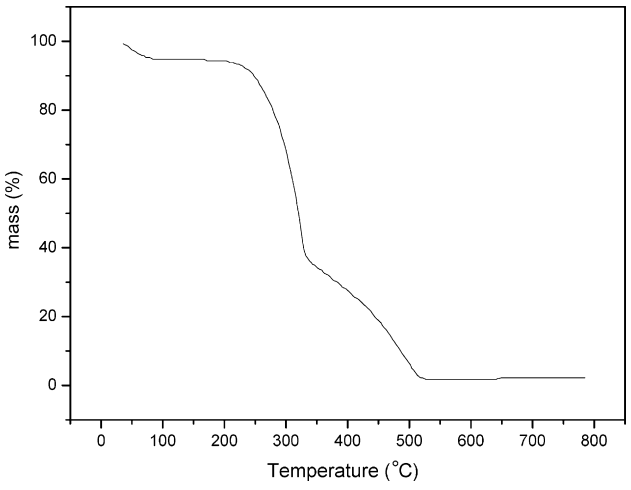

Fig. 1. TGA curve of *Luffa cylindrica* fiber.

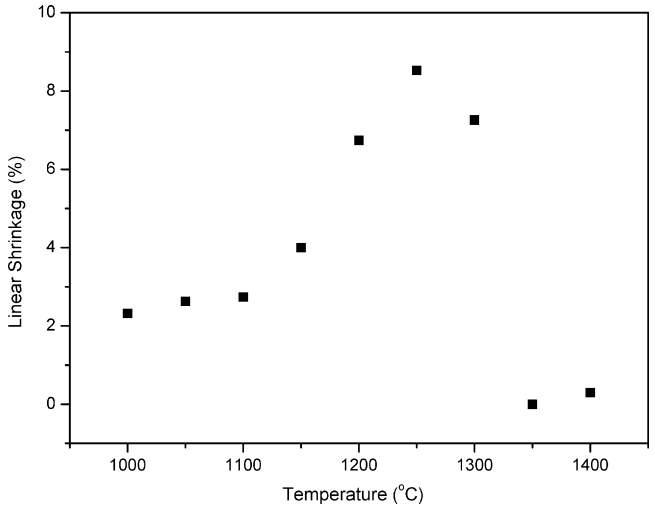

Fig. 2. Linear shrinkage of the compact bars with the temperatures.

particles, leading to a porous material formation [24]. Between 1100 and 1250 °C an increasing of the linear shrinkage values is observed, as it is related to viscosity values in this temperature range, its values must decrease. The filling of the porous layer of the material by the liquid phase is increased by the liquid phase property to spread better. After 1250 °C, the linear shrinkage decreases again and the visual inspection of the sintered samples showed that those sintered after 1250 °C were totally deformed. Therefore, best temperature range to sinter the material is the average temperature, 1175 °C, between 1100 and 1250 °C, in which the linear shrinkage values are higher than 515 °C, the lower temperature to decompose all organics from the vegetal fiber, and the samples do not deform with heating. Once determined the ideal sintering temperature, several samples were prepared at 1175 °C with different time intervals. Fig. 3 shows that linear shrinkage increases from 0 to 15 min, after that it is practically constant. Therefore, the best conditions to fire the reticulated samples are 1175 °C for times greater than 15 min. Visual inspection of samples prepared at 1175 °C for several periods showed that only the samples prepared for 120 min were rigid enough to be used as reticulated ceramic.

Fig. 4 shows XRD patterns of reticulated ceramic which were sintered at 1175 °C for 15, 30 and 120 min. One can observe that immediately at 15 min, the final crystalline phases, mullite (JCPDS 15-776) and cordierite (JCPDS 13-293) are already present. However, the absence of flatness on the XRD lines in Fig. 4a and b is an indicative of the amorphous materials presence, while the flatness of the XRD line in Fig. 4c is an indicative of material crystallinity. In the aluminosilicate phase diagram the only stable phase of mullite is the orthorhombic form, but sometimes it is possible to crystallize the tetragonal metastable phase. The unique difference between orthorhombic and tetragonal phases in the mullite XRD patterns is the splitted peak at $2\theta = 26.26$ of the orthorhombic phase [25]. Because of the overlap between the more intense peaks of mullite and cordierite ($2\theta = 26.26$ for mullite and $2\theta = 26.50$ for cordierite) it is not possible to conclude what mullite phase was crystallized.

Fig. 5 shows the SEM images of a polished ceramic reticulated sintered at 1175 °C for 120 min. One can clearly observe the presence of two different kinds of pores: (i) the first one with a spherical shape, ranging from 5 to 10 μm in diameter. This is present in larger amounts on the sample sintered for 120 min. Its presence is due to the incomplete sintering; (ii) the big one, measuring about 300 μm diameter, which is formed by the space left by the sponge's fiber eliminated during the thermal treatment. This bigger pore is connected by others in a way that all ceramic fibers of the reticulated ceramic have a similar channel in its interior, creating a network of the channels inside the network of the ceramic fibers.

Fig. 6 shows SEM images of a reticulated ceramic sintered at 1175 °C for 120 min. After the sintering step the sample was polished and superficially attacked with an aqueous solution of hydrofluoric acid 0.1% (v/v) for 10 s. During the SEM analysis the surface was analyzed with EDS (energy dispersive X-ray spectroscopy). Fig. 4 shows that this sample is constituted of mullite and cordierite and EDS analysis demonstrated that

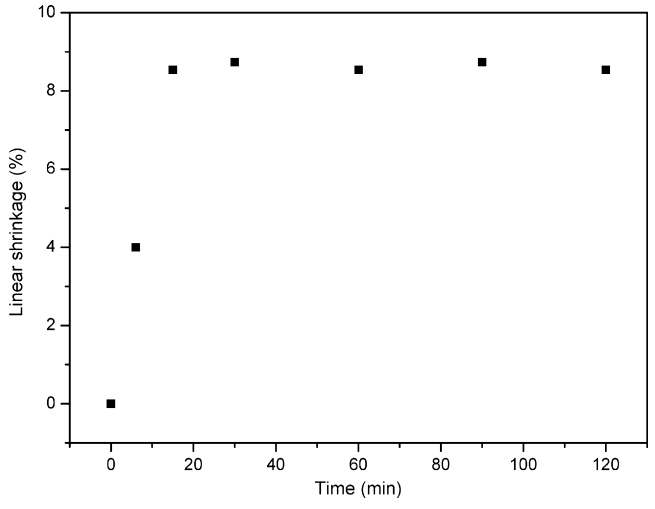

Fig. 3. Linear shrinkage of the compact bars calcinated at 1175 °C with time.

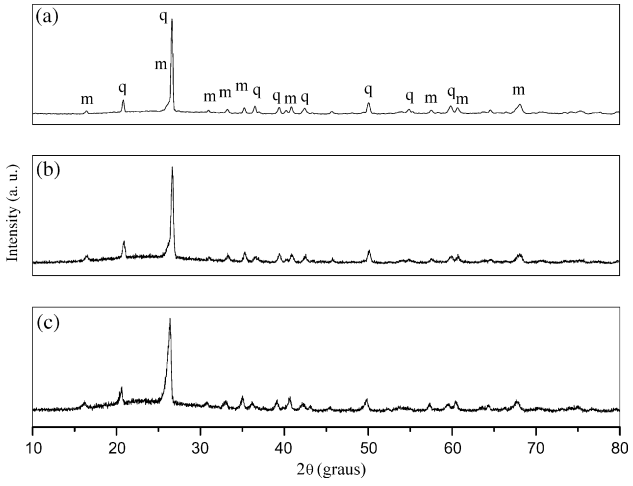

Fig. 4. XRD patterns of ceramic reticulated sintered at 1175 °C for 15 min (c), 30 min (b) and 120 min (a). Labels: m = mullite and q = cordierite.

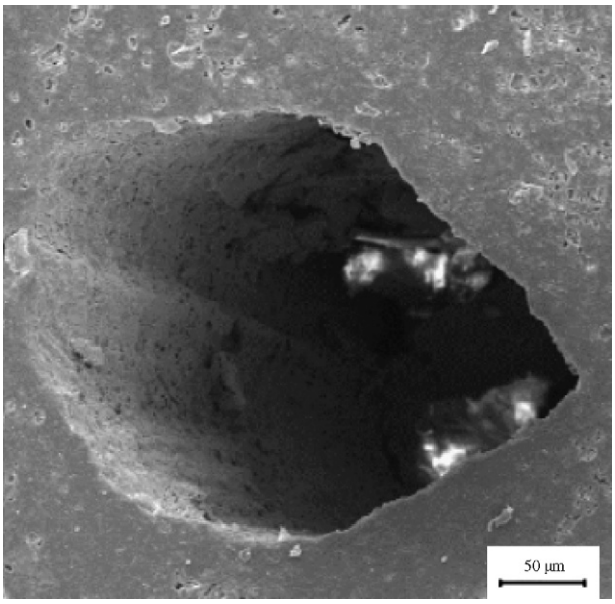

Fig. 5. SEM images of a polished surface of reticulated ceramic treated at 1175 °C for 120 min.

those acicular (whiskers) grains formed are the mullite phase, while the compact grains are created by the cordierite phase. Generally, the whiskers in the bulk material increase the mechanical resistance of the ceramic body and possibly be responsible for the mechanical stability of the ceramic fiber.

The apparent density of the reticulated ceramic was measured by Archimedes method. While the density of the reticulated body is (0.8 ± 0.2) g/cm^3, those related only to the wall of the reticulated ceramic is 2.79 g/cm^3. Therefore, volumetric fraction of voids is about 71% (v/v).

Fig. 7 shows an image of a partial portion of vegetal sponge, *L. cylindrica,* used to make the reticulated ceramic in Figs. 8 and 9. The reticulated ceramic maintains most of the form of the vegetal sponge. As in the vegetal structure, in the reticulated ceramic the fibers are arranged in a tridimensional network, where the fibers link to each other randomly. In the regions where the natural fibers were too close, some plates were formed in the ceramic reticulo. This randomness leads to the formation of a highly anisotropic structure, which is very convenient for a material designed to be used as filter or catalyst support.

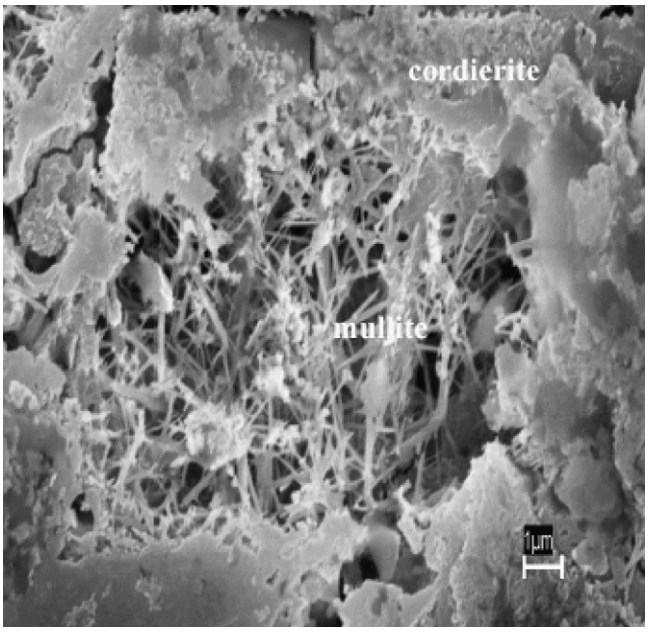

Fig. 6. SEM micrograph of a piece of reticulated ceramic attacked with HF.

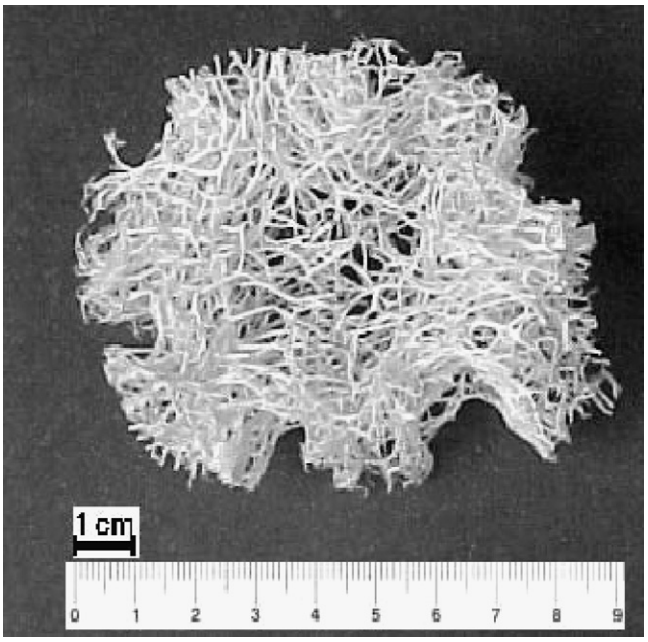

Fig. 7. Optical photograph of a piece of *L. cylindrica* used for reticulated ceramic preparation.

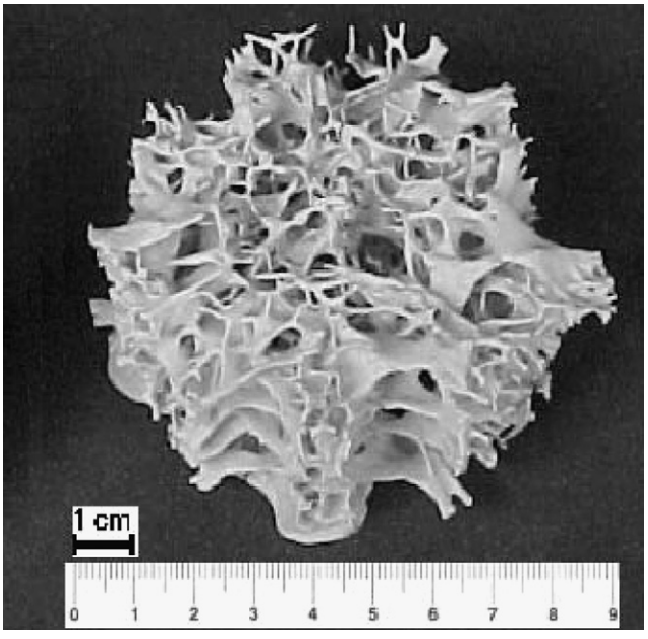

Fig. 8. Optical photograph of reticulated ceramic prepared with *L. cylindrica* showed in Fig. 7.

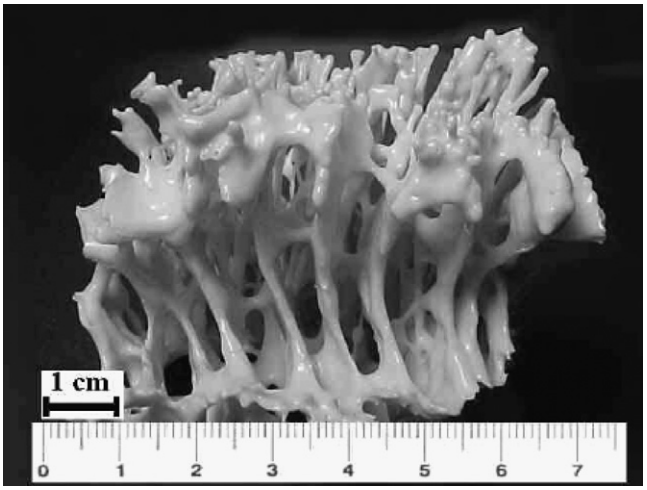

Fig. 9. Optical photograph of a lateral view of the reticulated ceramic in Fig. 8.

4. Conclusion

The polimeric sponge method was used to obtain reticulated ceramic in milimetric scale degree (5–10 mm) using a vegetal sponge, *L. cylindrica* specie as a template. The combination of the clay, K-feldspar and sand promotes an ideal plasticity to slurry, leading to the formation of reticulated sintered, without any apparent breakage and deformations. The morphology of the reticulated ceramic is identical to the vegetal sponge used as templating. Like the template structure, the reticulated ceramic has a tridimensional structure, where the ceramic fibers randomly link to each other. The best set of sintering time and temperature was 120 min at 1175 °C. In this condiction the reticulation was constituted of cordierite and mullite whiskers.

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