



## Full Length Article

# Structural and surface functionality changes in reticulated vitreous carbon produced from poly(furfuryl alcohol) with sodium hydroxide additions



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## ABSTRACT

The use of sodium hydroxide to neutralize the acid catalyst increases the storage life of poly(furfuryl alcohol) (PFA) resin avoiding its continuous polymerization. In this work, a concentrated sodium hydroxide solution (NaOH) was added directly to the PFA resin in order to minimize the production of wastes generated when PFA is washed with diluted basic solution. Thus, different amounts of this concentrated basic solution were added to the resin up to reaching pH values of around 3, 5, 7, and 9. From these four types of modified PFA two sample sets of reticulated vitreous carbon (RVC) were processed and heat treated at two different temperatures (1000 and 1700 °C). A correlation among cross-link density of PFA and RVC morphology, structural ordering and surface functionalities was systematically studied using Fourier transform infrared spectroscopy, scanning electron microscopy, Raman spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy techniques. The PFA neutralization (pH 7) led to its higher polymerization degree, promoting a crystallinity decrease on RVC treated at 1000 °C as well as its highest percentages of carboxylic groups on surface. A NaOH excess (pH 9) substantially increased the RVC oxygen content, but its crystallinity remained similar to those for samples from pH 3 and 5 treated at 1000 °C, probably due to the reduced presence of carboxylic group and the lower polymerization degree of its cured resin. Samples with pH 3 and 5 heat treated at 1000 and 1700 °C can be considered the most ordered which indicated that small quantities of NaOH may be advantageous to minimize continuous polymerization of PFA resin increasing its storage life and improving RVC microstructure.

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## 1. Introduction

The preparation of carbon materials using poly(furfuryl alcohol) (PFA) has been extensively explored in many research papers [1–3]. With a growing concern about using materials obtained from renewable resources of low cost and accessibility, furan oligomers are an alternative to obtain polymers that present broad industrial application. Thus, furfuryl alcohol is the most important furan monomer used as precursor to different resin types [4,5] and carbon materials such as nanostructured carbons and nanocomposites [6–9], micro and nanoporous carbon [10–14], glassy carbon [3,15–17], among others. PFA can be obtained from a

polycondensation reaction of furfuryl alcohol catalyzed by acids. Due to the furan ring great reactivity, curing and carbonization speed of furan resins are always faster compared to those of aromatic rings [18]. To avoid a violent reaction, the synthesis of PFA resin is carried out at low temperature (from 0 to 25 °C) and reaction time of up to 24 h [19–22]. The synthesis reaction can be finalized by cooling and neutralization to obtain the appropriate viscosity for the chosen application. In order to neutralize the acid catalyst, a solution of sodium hydroxide may be used to avoid continuous polymerization of PFA, increasing its storage life [20,22]. Some authors report that the neutralization process is slow and the PFA resin is usually washed several times with a diluted basic solution to avoid the emulsification [19,20]. However, this process generates toxic wastes due to the presence of monomers and PFA chains with low molecular weight. As a novelty of this work, it is proposed the neutralization of PFA with a minimum amount

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of concentrated NaOH solution which would avoid waste production. Also, the influence of this base on the crystalline structure and surface functionalities on vitreous carbon processed from this PFA must be investigated.

Vitreous carbon (or glassy carbon) is a form of carbon produced by the pyrolysis of an aromatic polymer, generally a phenolic or a PFA resin [16,23]. Reticulated vitreous carbon (RVC) is a porous foam-like structure and one of the most commonly carbon material used as electrode due mainly to the presence of many accessible pores with controlled sizes and high surface area, in addition to several other characteristics such as high chemical and thermal stabilities, catalytic properties, light weight, and low cost [2,23–27]. Normally, metals and alkali metals are added to non-graphitizing carbons in order to promote catalytic graphitization upon annealing [14,28–31]. The presence of sodium hydroxide can be evaluated as filler, which will affect the cross-link density of PFA and, consequently, the carbon properties and structural ordering processed from it. The carbon surface chemistry also influences many properties of carbon materials such as wetting, adsorption, catalysis, and electrochemical response [32–34]. As reported by Collins et al. [34], surface oxygen groups (SOG) are responsible for structure change, contributing to the partial graphitization process. However, SOG concentration in excess promotes graphite-like disorder. The structural influence of surface functionalities is rarely correlated with Raman or XRD. In this sense, the connection between Raman, XRD and surface functionalities results as well as among carbon material processing parameters is necessary for a complete understanding of their crystallite dimensions, graphitic-order, reactivity, and the structural influence of edge-site composition [34].

In this work the PFA resin acid catalyst was neutralized by adding different amounts of concentrated NaOH solution. Thus, our objective was to evaluate how this basic solution addition, which influences the cross-link density of cured PFA, can affect the processed RVC morphology, microstructure, and surface functionalities. To our knowledge, there are no papers in the literature that have tried to neutralize the PFA resin with a concentrated solution of NaOH and have showed a relationship between NaOH proportion in the PFA and the properties of processed carbon material. RVC was prepared using PFA resin with different amounts of concentrated sodium hydroxide solution until reaching pH of around 3, 5, 7 and 9. These samples were cured and subsequently submitted to heat treatment temperature (HTT) of 1000 and 1700 °C in order to obtain two sample sets with different graphitization indexes as a function of the PFA pH. All samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, XRD, and scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Poly(furfuryl alcohol) with different sodium hydroxide amounts

PFA was synthesized according to the previously described procedure [35], using furfuryl alcohol (Fluka) and diluted sulfuric acid solution (Fmaia) ( $0.5 \text{ mol L}^{-1}$ ) as catalyst. The acid PFA resin (pH ~ 3) obtained after partial polymerization was distilled in a rotary evaporator at a reduced pressure until reaching moisture below 2 wt%. The resin was then separated in four portions to prepare resins with different pH values (pH 3, 5, 7 and 9). The pH of the resin was varied by adding a concentrated solution of sodium hydroxide ( $2.0 \text{ mol L}^{-1}$ ) until reaching the desired values without occurs emulsification. The resin pH control was accomplished by directly measuring the resin with a pH meter from Methrom 827 pH Lab, with a glass pH combination electrode (Unitrode). PFA viscos-

ity varied from 12.9 Pas (pH 9 resin) to 21.0 Pas (pH 3 resin) at 25 °C. These measurements were performed in a Brookfield viscometer, model RV DV-II + Pro, with a SC4-34 spindle, using a shear rate of  $8 \text{ s}^{-1}$ , torque at 60.3% for pH 9 resin and shear rate of  $6 \text{ s}^{-1}$ , torque at 65.6% for pH 3 resin.

### 2.2. Reticulated vitreous carbon processing

Polyurethane foams with 70 pores per inch (ppi) were kindly donated by Sanko Espumas. The foams were cut into dimensions of 18 cm x 8 cm, followed by impregnation of about 20 g of PFA resins containing different quantities of sodium hydroxide. The resin was catalyzed with 3 w/w% of diluted *p*-toluenesulfonic acid (60 w/v%). Impregnated foams were cured in an oven for 1 h in the following temperatures: 50, 70, 90, 110, 130 °C. HTT of 1000 °C was carried out in a tube furnace from room temperature at heating rate of 1 °C/min in N<sub>2</sub> atmosphere reaching the maximum for 1 h up to its cooling down to room temperature. HTT of 1700 °C was carried out in similar way, except for using a heating rate of 5 °C/min. Characterizations are included in the Supplementary material.

## 3. Results

### 3.1. FTIR analysis

Fig. 1a shows the cured PFA FTIR spectra with different sodium hydroxide amounts. The band at  $3400 \text{ cm}^{-1}$  increased as a function of NaOH amount increase related to OH stretching [36]. Other characteristic bands of PFA are [19,37–40]: the bands at 2920 and  $1430 \text{ cm}^{-1}$  related to the aliphatic segments presence; the band at  $1715 \text{ cm}^{-1}$  due to the occurrence of some ring opening of furan ring; the band at  $1560 \text{ cm}^{-1}$  assigned to conjugated C=C species; the bands at 1506, 1157 and  $1010 \text{ cm}^{-1}$  attributed to furan ring; the band at  $1360 \text{ cm}^{-1}$  due to C–C or CO stretching; the band at  $1220 \text{ cm}^{-1}$  related to C–O from the alcohol or C–O–C of furan ring; and the band at  $780 \text{ cm}^{-1}$  characteristic of 2,5-disubstituted furan ring. The reaction progress ( $\alpha$ ) can be evaluated by the quotient among integrated intensity of primitive bands, i.e.,  $\alpha = I_{736} + I_{750} / (I_{782} + I_{790} + I_{803})$  [40]. The smaller this quotient, the farther the reaction has progressed. The decomposed bands at 736, 751, 782, 790, and  $803 \text{ cm}^{-1}$  were determined by spectra deconvolution in the interval from 700 to  $850 \text{ cm}^{-1}$  (Fig. 1b), using Gaussian shaped bands for the spectrum in absorbance. The calculated  $\alpha$  values for pH 3, 5, 7, and 9 are 0.82, 0.79, 0.72, and 0.86, respectively. From these results, it can be inferred that sample pH7 presented the highest polymerization degree, since it had the lowest  $\alpha$  value, followed by sample pH 5, 3 and 9 in descending order of polymerization degree.

### 3.2. Morphological and surface characterizations

RVC obtained from PFA resin with different NaOH additions for HTT at 1000 and 1700 °C were characterized by FEG-SEM images of their stems surfaces in two different magnifications (2000x and 10000x). Fig. 2 shows representative micrographs of RVC in which the nomenclature was created concerning the adjusted pH for each resin followed by its related RVC HTT values. RVC images heat treated at 1000 °C (RVC1000), indicate that pH3\_1000 sample present a uniform texture resulted from good polyurethane foam impregnations. Sample pH5\_1000 present a similar texture but at higher magnification it is possible to notice some irregular surface. On the other hand, pH7\_1000 and pH9\_1000 present morphologies significantly modified with higher roughness, attributed to the higher inclusions of sodium hydroxide. Some regions with agglomerates of NaOH and small pores can be seen in pH7\_1000 sample and small crystals are visible over the whole pH9\_1000 surface.

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