

Viscosity, pH, and Moisture Effect in the Porosity of Poly(furfuryl alcohol)

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ABSTRACT: The poly(furfuryl alcohol) is highly indicated to obtain advanced carbonaceous materials due mainly to its good carbon yield (around 50%) and a controllable cure reaction. In the processing of some carbonaceous materials, such as monolithic vitreous carbon, it is necessary to make sure that the material has the smallest porosity to be used in nobler applications such as heart valves and aerospace integrated systems. In this manuscript, a design of experiments was used to study the influence of viscosity, pH, and moisture in the porosity of the cured material. This study shows that the moisture exerts a significant influence on the porosity and the trend of the results lead to conclude that lower viscosity and moisture, and the use of non-neutralized poly(furfuryl alcohol) resins lead to obtain materials with better quality. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

The poly(furfuryl alcohol) (PFA) is a thermoset polymer obtained from the polycondensation of its monomer, furfuryl alcohol (FA), which is usually produced from renewable sources, such as bagasse from sugar cane, corn and rice husk, by a simple reduction process of furfural.^{1,2}

The interest in obtaining the PFA is due to the fact of presenting a high density of crosslinks when cured which, when subjected to heat treatment of carbonization up to at least 1000°C in the absence of oxygen, results in a type of nongraphitizing material called vitreous carbon. The vitreous carbon has, as main features, good mechanical strength, good thermal and electrical conductivities, it is biocompatible, and it presents low density.^{3–5}

The monolithic form of vitreous carbon is characterized by the presence of intrinsic micro and mesopores, originating from the turbostratic structure that reflects the features of thermosetting resin structure.^{5–7} As the pyrolysis temperature of PFA is increased, the mesoporosity can disappear and the microporo-

sity is retained due to the formation of polyaromatics domains.⁸ There is also the possibility of macropores to appear, resulting from the preparation of the PFA and the curing conditions. The necessity to obtain materials with a lower porosity can allow the application of monolithic vitreous carbon (MVC) in various fields such as aerospace, medical, electronics, chemical, and steel production.^{4,5,9}

In previous works,^{3,10,11} our group has been working with commercial PFA resins that didn't have uniform characteristics of viscosity, pH, and moisture. This lack of uniformity requires constant processing adjustments in every new lot to be used to obtain the vitreous carbon. Working with the synthesis of this resin allows adjusting the parameters according to the necessity of the application.

The aim of this work is the search for a rigid control of the processing parameters for obtaining monolithic vitreous carbon starting from the establishment of the best parameters for the synthesis of PFA to avoid the formation of macropores in the cured resin. Because of the lack of systematic studies concerning the synthesis of PFA for use in the processing of MVC, a design

Table I. Levels of Variable Viscosity (A), pH (B), and Moisture (C)

Variable	Levels	
	Low (-)	High (+)
A Viscosity (mPa s ⁻¹)	~1500	~3500
B pH	~3	~7
C Moisture (%)	<2	~5

of experiments 2³ was used in this work to verify the influence of viscosity, pH, and moisture in the polymerized resin. Based on the best established parameters it is possible to synthesize a resin that ensures the integrity of the carbonized material. The experimental design reduces the time and the experiments' cost, in addition presenting reliable results, even with a smaller number of tests.¹²

EXPERIMENTAL

In this manuscript, the variables selected to optimize the process of the vitreous carbon were: (a) viscosity between 1000–1500 mPa s⁻¹ and 3000–3500 mPa s⁻¹; (b) pH between 3 and 7, and (c) moisture between 2 and 5% of the synthesized PFA. The two levels selected for the viscosity variation are based on the range of working conditions which are more favorable in the processing of vitreous carbon, because there is a greater amount of free FA in the resin below 1000 mPa s⁻¹, which increases the exothermal reaction during the curing process, whereas viscosities above 3500 mPa s⁻¹ hinder the release of air bubbles and volatiles during the processing.¹⁰ The values of pH 3 and 7 are related to the acid resin, obtained after the synthesis, and the resin after neutralization with sodium hydroxide, respectively. The moisture content of about 5 and 2% are the obtained values before and after the distillation of the synthesized resin, respectively.

Synthesis of Poly(furfuryl alcohol) Resin

The polymerization of furfuryl alcohol (supplied by Fluka, purity >98.0%) was conducted in a three-necked flask under reflux and magnetic stirring. A dilute aqueous solution of sulfuric acid (supplied by Fmaia, purity 97.0%), (0.5 mol L⁻¹) was used as the catalyst in the following proportions: [FA]/[acid solution] = 140. With the purpose of obtaining the values of resins with viscosities around 1500 and 3500 mPa s⁻¹, the reaction time lasted from 1 to 6 h, monitoring the temperature of the bath as well as the reaction, so that the system does not come into boiling. After the conclusion of the synthesis, the resin was neutralized with a concentrated solution of sodium hydroxide (supplied by Dinâmica, purity 97.0%), (2.5 mol L⁻¹). The next step was to remove the excess of water originating from the synthesis and the neutralization solution in a rotary evaporator at a reduced pressure of 700 mmHg for 40 min at 50°C. To make this distillation become more efficient, 10% w/w of anhydrous methanol (supplied by Mallinckrodt, purity >99.8%) was added into the resin. All the chemicals were used as received.

Characterization of the Synthesized Resin

The PFA synthesized samples were assessed by using Fourier transform infrared spectroscopy (FT-IR), utilizing a spectropho-

tometer from Perkin Elmer Instruments, Spectrum 100 model, using the attenuated total reflectance (ATR) technique.

Thermogravimetric analyses were performed in a Seiko equipment, model TG/DTA 6200, at a heating rate of 10°C min⁻¹ and under constant nitrogen flow (100 mL min⁻¹).

The control of viscosity of the synthesized resin was analyzed by using a Brookfield viscometer, model RV DV-II + Pro, spindle SC4-27.

The control of pH values of the resin samples was accomplished through directly measuring the resin with a pH meter of Pensalab Metrohm, model 827 pH lab, adapted with a glass pH combination electrode (Unitrode). These measurements were performed on resin samples after the synthesis and after the neutralization with the basic solution.

The moisture from the resin newly synthesized and distilled was determined using a Karl Fischer titrator Titrimo plus 870 from Metrohm Pensalab.

Design of Experiments 2³

The design of experiments used in this work is presented in Tables I and II. Table I shows the values of viscosity, pH, and moisture level in each study. Eight combinations were altogether conducted (Table II) and the response variable chosen was the porosity because it is an important parameter in assessing the quality of the material to be obtained. All the statistical analyses were processed using the MINITAB[®] software version 14.

Curing of the Poly(furfuryl alcohol) Resin

Samples of acid and neutral PFA obtained were respectively catalyzed by the addition of 2 and 5% (w/w) of an aqueous solution of *p*-toluenesulfonic acid (60% w/v). These contents were determined from the test of catalyst, which consists of inspecting the appearance of the resin 24 h after the addition of *p*-toluenesulfonic acid. The concentration of catalyst was considered satisfactory when the resin presented a slightly rubbery appearance after 24 h of polymerization. The choice of this parameter is based on previous works of the group^{11,13} and it ensures a slow cure allowing volatiles to be released while the polymer is not fully rigid. After this step, the catalyzed resins were centrifuged for 15 min to remove air bubbles introduced into the resin during the homogenization step by manual mixing of the catalyst. Then, the samples were cured in an oven, according to the following thermal cycle: 50°C for 10 h, followed by new thermal isotherms steps of 2 h in each of the following temperatures: 80, 100, and 150°C. These temperature values were based on the results obtained by pressurized differential scanning calorimetry (PDSC). Analyses of PDSC were carried out in pressurized equipment from TA Instruments DSC 2910, fitted with a pressure cell. Approximately 2 mg of

Table II. Eight Resins Combined Studied with the Respective Variables

Variable	1	2	3	4	5	6	7	8
A	-	+	-	+	-	+	-	+
B	-	-	+	+	-	-	+	+
C	-	-	-	-	+	+	+	+

Table III. Values of Viscosity (A), pH (B), and Moisture (C) of the Synthesized Resins

Resin	A	B	C	Viscosity (mPa s ⁻¹)	pH	Moisture (%)
1	-	-	-	1233	3.0	1.5
2	+	-	-	3558	4.6	1.1
3	-	+	-	1506	6.8	1.8
4	+	+	-	3662	6.9	1.3
5	-	-	+	1173	1.9	4.6
6	+	-	+	3034	3.5	6.5
7	-	+	+	1561	7.4	4.5
8	+	+	+	3002	7.0	6.7

catalyzed resin samples were used, with a heating rate of 10°C min⁻¹ and N₂ pressure of 2.1 MPa in the temperature ranging between 30 and 250°C.

Characterization of the Cured Resin

Starting from the cured samples, the carbon yield (carbon residue after carbonization heat treatment of organic materials) was determined based on ASTM D3172-07a and the characterization by optical microscopy using a Nikon microscope, model EPIPHOT 200. For the image analysis, the Image J program was used.

RESULTS AND DISCUSSION

The experimental values of viscosity, pH, and moisture of the synthesized PFA are presented in Table III. A viscosity range of 1000–1500 mPa s⁻¹ (low level) and 3000–3500 mPa s⁻¹ (high level) was tried. However, in some cases, these values were exceeded due to the difficulty in controlling this parameter during the synthesis, so the reaction was concluded by the variation of time (1–6 h). During the distillation step, heating and water removal can also affect the final viscosity of the resin.

In most of the characterizations carried out only the results obtained with the resin 1 and 8 are shown. Because of their opposite characteristics of viscosity, pH, and moisture it is easier to notice the variations caused in these two resins.

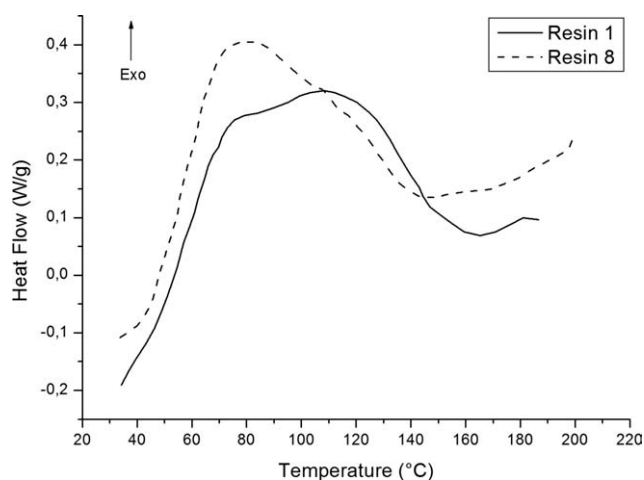


Figure 1. PDSC curves of resin 1 and 8.

Table IV. Peak, Onset, and Endset Temperatures, and Enthalpy Variation of Resins 1 and 8

Resin	Onset temperature (°C)	Peak temperature (°C)	Endset temperature (°C)	ΔH (J g ⁻¹)
1	47	98	160	158
8	43	79	144	127

In this article, the PDSC was used since the cure of PFA occurs in the same range where there is the release of volatiles, as shown in Figure 1. The results of PDSC defined the most appropriate cure cycle for the synthesized PFA, based on literature,¹⁴ which shows a slower polymerization held near the onset temperature, resulting in a material with a lower porosity. Table IV presents the results obtained from the onset temperature, peak, endset, as well as the enthalpy variation of resin 1 and 8.

The onset and endset temperatures are characterized, respectively, as the starting and the ending extrapolated cure temperatures obtained from crossing the established baseline and the beginning of thermal curve deflection. Thus, the cure of all samples was started at 50°C indicating a slower cure. As intermediate points of this process, two values, 80 and 100°C, close to the most exothermic reaction were adopted, and finally, to ensure a complete and homogeneous cure of the material, it was decided to finalize the cure at 150°C.

The neutralization helps to keep the resin with the initial established viscosity, increasing its durability, however it will need higher temperatures to start and finish the cure. Because of the neutralization of resin 8, 5% w/w of the catalyst *p*-toluenesulfonic acid was used instead of the 2% used for acid resin. In this way, the cure behavior can be adjusted with the catalyst percentage to get the same curing degree using the same thermal cycle.

Comparing the enthalpy results of resins 1 and 8, it is observed that resin 1 with lower viscosity has a higher reaction enthalpy. One possible cause for this behavior is the presence of free monomers in this sample, ready to polymerize, contributing to an increase in the exothermic reaction. The higher viscosity of the resin indicates that the polymerization reached a more advanced stage during the synthesis, making the reaction more easily controlled during the final cure.¹⁵

Table V summarizes the main results of the levels determined by moisture, ash, volatile matter, and carbon yield of resins 1 and 8 synthesized in this work. Such analyses were performed on cured resins ergo the moisture values differ from the values measured by Karl Fischer titration. The ash content is related to the presence of inorganic residue after carbonization, therefore the highest value found for resin 8 (0.44%) may be related to the presence of sodium hydroxide coming from the neutralization process. The volatile materials refer to the percentage of gaseous products and vapors of moisture in the sample, which are released under specific test conditions. Resin 1 and 8 showed a percentage of volatile matter of 52.6 and 56.3%,

Table V. Moisture, Ash, Volatile Matter, and Carbon Yield of the Synthesized Resins

Resin	% Moisture	% Ash	% Volatiles	% Carbon
1	1.99 ± 0.02	0.36 ± 0.02	52.60 ± 0.22	45.05 ± 0.16
8	1.68 ± 0.19	0.44 ± 0.02	56.29 ± 0.14	41.59 ± 0.07

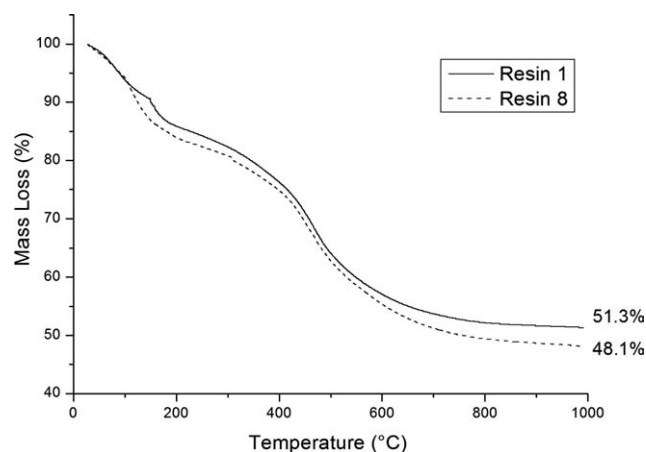
respectively. These values contributed to a lower carbon yield of resin 8, since the value of the fixed carbon is calculated by subtracting from 100 the resultant of the summation of percentage moisture, ash, and volatile matter.

The carbon yield is an important parameter in the search for materials with minimal flaws such as pores and cracks. Therefore, the higher carbon yield of resin 1 may contribute to the lower volumetric shrinkage of the material during the carbonization process reducing the occurrence of defects.

Another way of obtaining carbon yield is by using thermogravimetric analysis. Figure 2 shows that the carbon yield at 1000°C of resin 1 and 8 were 51.3 and 48.1%, respectively. Although these values were higher than those obtained by ASTM D3172-07a standard, the difference between resin 1 and 8 were retained at about 3%.

Both resins present a similar mass loss behavior which occurs mainly in the temperature range of 30–200°C, assigned to desiccation and CH₄ and, 400–600°C, attributed to the loss of CO, CO₂, CH₄, and H₂O. It can be observed the mass loss of resin 8 is bigger after 110 and 600°C. This is related to the presence of higher moisture and inorganic residue coming from the neutralization.

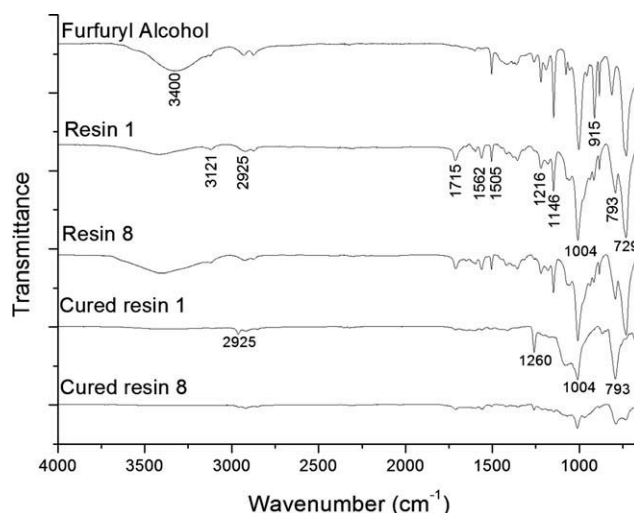
Figure 3 shows the FT-IR spectra of the FA monomer, the polymerized FA and cured resins 1 and 8. Figure 4 shows more probable structural models of PFA with specific moieties marked. It can be observed that the resins still present features of the FA spectrum and the main variations in the structure during the polymerization of FA, namely, the decrease in the band at 3400 and 915 cm⁻¹, which can be attributed to the OH stretch and unreacted FA, respectively, the weak band at 1715 cm⁻¹ can be related to the stretching vibration suggesting the

**Figure 2.** Thermogravimetric analyses of resin 1 and 8.

occurrence of some ring-opening due to the formation of dike-tonic structures (labeled A in Figure 4) and the band at 1562 cm⁻¹ assigned to conjugated C=C species (labeled E in Figure 4).^{16–19} Although the characteristics of viscosity, pH, and moisture of resins 1 and 8 are opposite, the spectra are similar and can be observed only in a more pronounced OH band in resin 8, which can be related to higher moisture and also the addition of NaOH. Others characteristic bands of PFA resin are the band at 3121 cm⁻¹ related to the C3 and C4 carbon (labeled F in Figure 4); 1505, 1146 and 729 cm⁻¹ attributed to furan ring and 1216 cm⁻¹ related to C—O from the alcohol or C—O—C of the furan ring.^{17–20} According to Burket et al. the —CH₃ terminated groups (labeled B in Figure 4) should appear at 1380 cm⁻¹.⁸

In the cured resins, there is a decrease in the intensity of all bands. It can be highlighted in the following bands from this spectra: 793 cm⁻¹ characteristic of 2,5-disubstituted furan ring (labeled C in Figure 4); 1004 cm⁻¹ attributed to the ν C—O of furan ring; 1260 cm⁻¹ related to the asymmetric and symmetric stretching vibration of =C—O—C groups belonging to 2-substituted furan rings and the weak band around 2925 cm⁻¹ suggesting the presence of methyl groups (labeled D in Figure 4).^{16–20} Resin 8 presents a reduced intensity of the bands compared to resin 1. This behavior may be related to the presence of NaOH from neutralization causing changes in the structure, which can lead to the appearance of cracks during the carbonization process of the vitreous carbon.

Figure 5 shows the representative micrographs of each type of synthesized resin and Table VI presents the results of porosity and average pore size obtained by image analysis. The pore size

**Figure 3.** IR spectra of the furfuryl alcohol, resin 1 and 8 liquid, and cured resins 1 and 8.

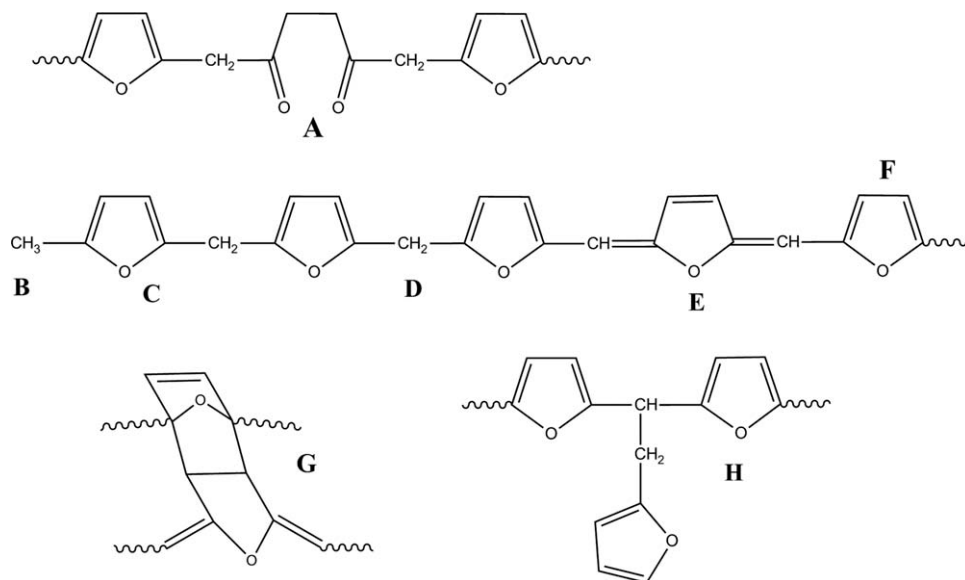


Figure 4. Models of structures found in PFA: (A) carbonyl group, (B) terminal methyl group, (C) 2, 5 carbons, (D) methylene bridge, (E) backbone conjugation, (F) 3, 4 carbons, (G) Diels–Alder reaction, (H) branched sequence.

was defined by Feret diameter, which is the length of the shaft that connects the farthest points of the particle perimeter. Because pores have dimensions with a high variability, the Feret diameter is an appropriate measure for this study.

It is observed that samples of resins 1 to 4, with moisture content <2%, have fewer pores and considering the standard deviation, the average pore sizes are very close. On the other hand, samples of resins 5–8, with moisture around 5%, have higher porosity, representing up to 43.3% of the analyzed surface and a substantial increase in the average pore size.

A Pareto chart of effects related to the porosity is shown in Figure 6, where the bar lengths are proportional to the absolute value of the estimated main effects. The vertical line corresponds to the 95% confidence interval and all the effects which exceed this line may be considered significant, as regards the response. In this study, just the moisture had a significant effect due to the evaporation of water during the curing process resulting in porosity. The positive sign of the effect estimated for the moisture showed that the porosity would be increased at a high level. Therefore, to avoid the porosity, low moisture should be used. Because any other variable was significant, it

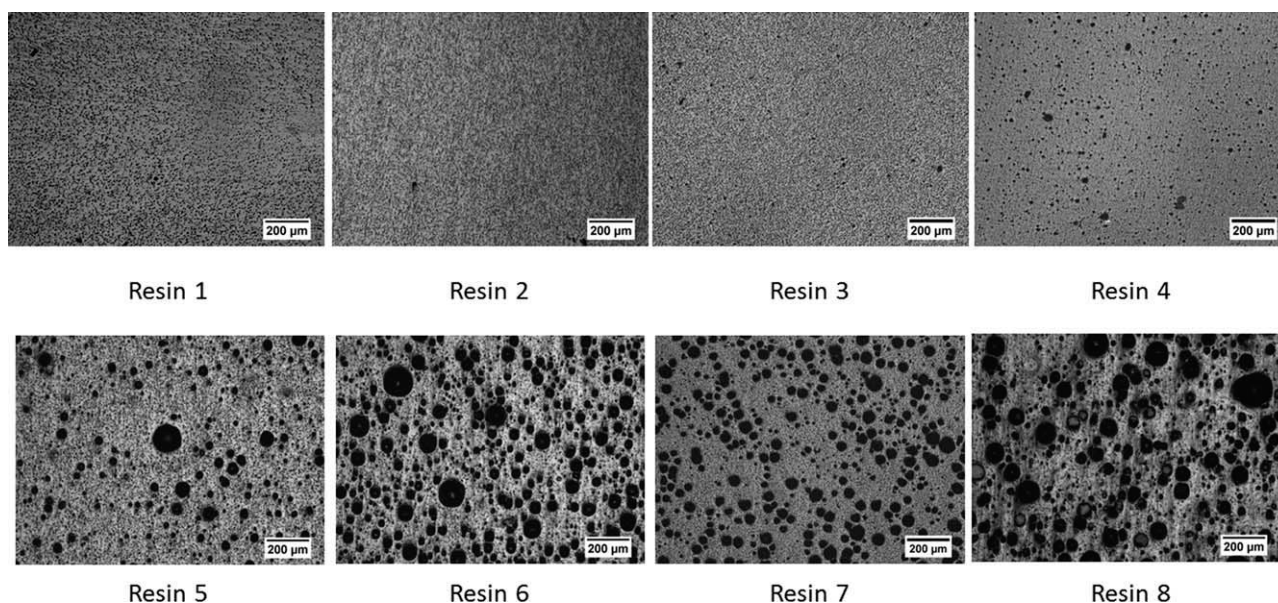


Figure 5. Micrographs of the cured resins.

Table VI. Results of Image Analysis Obtained from the Micrographs of the Eight Resins Analyzed

Resin	Parameters	
	Total porosity (%)	Average pore size (μm)
1	5.58 ± 2.84	10.19 ± 1.72
2	7.72 ± 3.46	10.10 ± 2.78
3	8.11 ± 3.06	9.47 ± 2.52
4	10.14 ± 1.34	13.27 ± 2.55
5	24.34 ± 4.03	49.15 ± 11.73
6	40.71 ± 1.85	126.25 ± 16.81
7	32.65 ± 5.65	81.90 ± 20.67
8	43.26 ± 3.65	194.40 ± 24.65

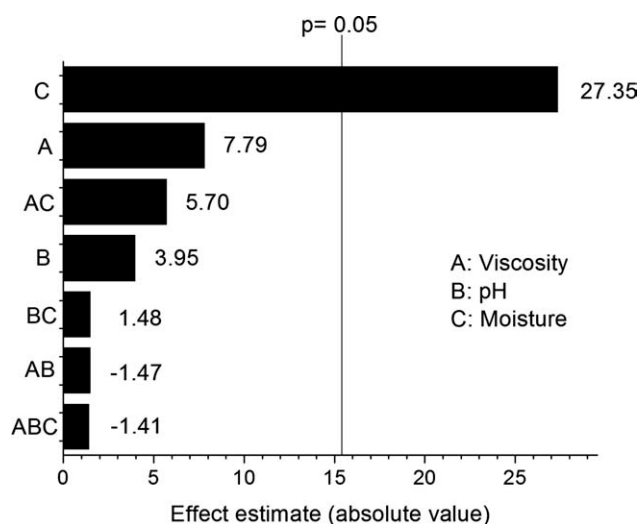
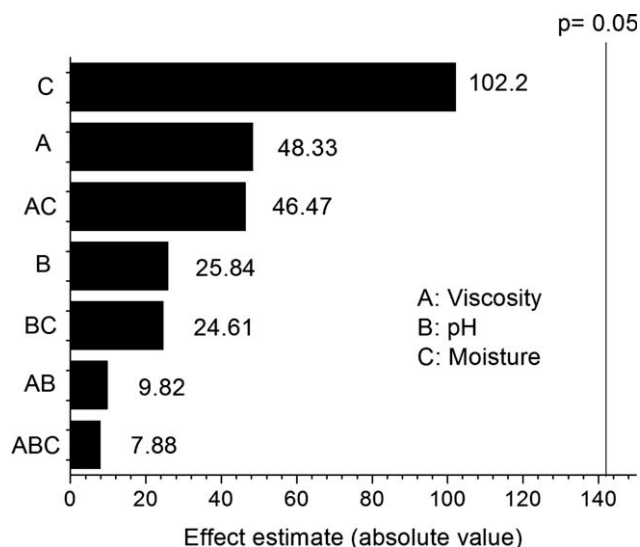
can be chosen to work in high or low level taking into account the value that has the lowest cost. However, the FT-IR analysis shows a modification in the structure of the neutralized cured resin, so in this case, it is advisable to work with the acid resin.

In the viscosity range studied, no statistical significance was observed. Perhaps the choice of lower viscosity would increase the relevance of this variable due to the tendency observed of lower porosity and average pore size for resins 5 and 7.

Figure 7 shows Pareto chart results related to the average pore size. In this case, no significant effect was observed since any effect reached the vertical line. However, the results show the same trend observed to the response porosity, that is, the relevance of moisture and the increasing response at the high level.

CONCLUSIONS

The PDSC analyses established the most appropriate cure cycle for the synthesized PFA resin. Through the image analysis of micrographs and design of experiments, it can be stated that

**Figure 6.** Pareto chart of main effects obtained for the response variable porosity.**Figure 7.** Pareto chart of main effects obtained for average pore size.

moisture is the most significant factor for the appearance of pores. Therefore, the distillation step is essential in the production of PFA. The viscosity was not a relevant variable in the range studied, but it shows a tendency of lower porosity and average pore size at lower viscosity. The FT-IR analysis shows a modification in the structure of the neutralized cured resin due mainly to the presence of NaOH, which can lead to the appearance of cracks during the carbonization process of vitreous carbon. According to the obtained results, it can be concluded that the use of PFA resins with viscosity, pH, and moisture in the established lower level results in materials with better quality.

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