Effect of Furfuryl Alcohol Addition on the Cure of Furfuryl Alcohol Resin Used in the Glassy Carbon Manufacture

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ABSTRACT: Glassy carbon can be manufactured practically without pores, named Monolithic Vitreous Carbon (MVC) or presenting up to 98% in transport pore volume, foam form, denominated Reticulated Vitreous Carbon (RVC). The glassy carbon processing is affected by some processing parameters, among them it can be cited the resin viscosity. The present work involves the optimization of RVC manufacture by monitoring the polyurethane (PU) foam impregnation with furfuryl alcohol resin with different viscosity values, which were obtained by dilution of the resin with different amounts of furfuryl alcohol. The resin samples used in the PU impregnation were characterized by thermal and rheological analyses. These results were correlated with scanning electron microscopy observations and compression test results of the impregnated polyurethane foam. The results show that the rheological behavior of the resin has significant influence on the polymerization step, affecting the homogeneity of impregnated foam and, consequently, its final properties, mainly the mechanical one. The impregnated foam prepared with the furfuryl alcohol resin diluted with 10% of furfuryl alcohol (η = 11.4 Pa s) showed higher compression values (0.26 MPa). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2274–2281, 2007

Key words: reticulated vitreous carbon; furfuryl alcohol resin; thermal analyses; rheological analyses

INTRODUCTION

The use of glassy carbon material in different applications involving medical, electrochemical, and aerospace areas has widely increased in the last years.[1–3] This material is obtained through the carbonization heat treatment of cured thermoset resins, producing artifacts with complex shapes for different uses. Thermoset resins such as phenolic and furfuryl alcohol resins have been used as raw materials for the glassy carbon manufacture using, generally, almost the same preparation procedure.[4–10]

Although named glassy carbon, this material can not be considered a glass from its crystallographic characteristics, because this material presents biorientation arrangement of its carbon atoms forming graphitic planes. The glassy denomination comes from the glassy appearance of the material after polishing and also due to its brittle fracture that is similar to the glass (conchoidal type). This carbon material class presents closed porosity in the monolithic form (MVC), characterized by intrinsic presence of micro (<2 nm) and mesopores (2–50 nm).[7–10] Another type of glassy carbon, called reticulated glassy carbon or Reticulated Vitreous Carbon (RVC) is characterized by the presence of transport macropores (>50 nm), which reach up to 98% in volume of the carbon material.

This material can be manufactured by different ways,[10] but in this study the porous volume is obtained by the heat treatment, in inert atmosphere, of porous polymeric substrates impregnated with thermoset resin that presents high carbon yield (above 40%, w/w). Porous carbons with porosity above 50% in volume are useful for numerous non-structural applications, such as electrodes, catalysts, catalyst support, filters, chemical absorbers, molecular sieves, membranes, dental and surgical prosthetic devices, and thermal insulators.[10–18]

Nowadays, a common thermoset resin used for the glassy carbon production is the phenolic one.[10–18] However, the use of furfuryl alcohol resin has presented some advantages in the glassy carbon manufacture because it shows more controlled cure kinetics and a lower gel temperature ($\sim$ 60°C).[19–24]

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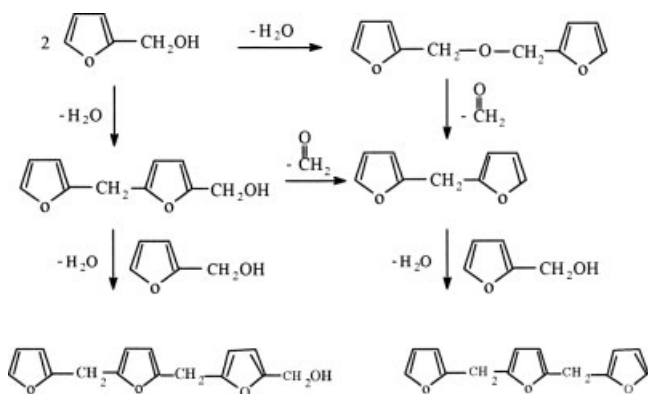
Figure 1 Dunlop and Peters mechanism scheme for furfuryl alcohol resin synthesis.[3,7,10]

The synthesis route of this resin is based on the acid catalysis of furfuryl alcohol and the reaction mechanism of this reaction was suggested by Dunlop and Peters.[24] The furfuryl alcohol resin synthesis involves an alcohol group from the furfuryl alcohol molecule with an active hydrogen of an aromatic ring of adjacent molecule, forming the di-furfuryl alcohol, as depicted in Figure 1.[21] This polymerization is too susceptible to the synthesis parameters, which affect the final characteristics of the resin, mainly its viscosity and its cure kinetics.

The knowledge of certain physical-chemical characteristics of the resin, such as its thermal and rheological behaviors, supports the establishment of the best processing parameters of the resin cure. These parameters determine the final properties (such as density, mechanical resistance, and electrical conductivity) and also the morphological aspects (porous size and distribution) of the processed glassy carbon.[21,25–27] Among the resin characteristics that influence its processing it can be cited its viscosity. An adequate control of this parameter facilitates the volatile release, favors an efficient impregnation of the porous substrates in the RVC processing and allows an adequate resin casting in the MVC manufacture. The viscosity control can be made during the resin synthesis or by diluting the resin with different amounts of an adequate solvent. The latter procedure is frequently used to take advantage of stocked resin that can shift its molar weight distribution to higher values increasing, consequently, its dynamic viscosity.

This work evaluates the influence of furfuryl alcohol addition into the furfuryl alcohol resin used in the impregnation of polyurethane foam, being the impregnated foam an intermediate in the RVC processing. Thermal and rheological properties of furfuryl alcohol resin are correlated with morphological aspects of the impregnated foam.

MATERIALS AND METHODS

Materials

The used furfuryl alcohol resin sample was supplied by Cersa Company (from Brazil), with initial dynamic viscosity of 17,000 mPa s. This sample was diluted with 0, 5, 10, 15, 20, and 25% (w/w) of furfuryl alcohol. All prepared samples were catalyzed by addition of 3.5% (w/w) of aqueous solution of p-toluenesulfonic acid (p-TSA - 60%, w/v).

Three different types of polyurethane foams, produced by Bulpren from German, were used as substrate to be impregnated. The types are classified in small pores (between 400 and 600 μm) named ''S'' (40 ppi—pores per inch), intermediate pores (between 700 and 900 μm) named ''I'' (30 ppi) and large pores (between 900 and 1800 μm) codified as ''L'' (10 ppi).

Experimental

The furfuryl alcohol resin samples, diluted with different furfuryl alcohol contents, were characterized by thermal and rheological analyses. The thermal analyses were carried out by Differential Scanning Calorimetry (DSC) performed in a Pyris equipment and by thermogravimetric analyses (TG) with a module TGA 7 both from Perkin Elmer, at a heating rate of 10°C/min and under a constant nitrogen flow (20 mL/min). This heating rate was defined in previous work.[22,23] Both, DSC and TGA analyses were performed in triplicate for each condition, showing good reproducibility. The rheological analyses were made in a controlled stress rheometer from Rheometric Scientific, series SR 5 using parallel plates, constant frequency of 1 rad/s, heating rate of 5°C/min and tension of 500 Pa s. The dynamic viscosity analyses were performed using a Brookfield viscometer model DV-II and a number 18-spindle.

Based on these analyses it was chosen the most appropriate furfuryl alcohol resin viscosity to be used in the impregnation step. For this, the three polyurethane foams were impregnated by using the dip coating technique as depicted in Figure 2. After the impregnation, the samples of polyurethane foam impregnated with furfuryl alcohol resin were heated from room temperature (nearly 25°C) up to 60°C at 10°C/h, holding at this temperature for 2 h. Afterwards, the temperature was elevated up to 80°C, maintained at this temperature for more 2 h, then cooled until the room temperature.

The impregnated polyurethane foam samples were characterized by scanning electron microscopy (SEM) using a Zeiss West Germany, model DSM 950. The images were used to determine the medium pore size. Using an Instron test machine model TM
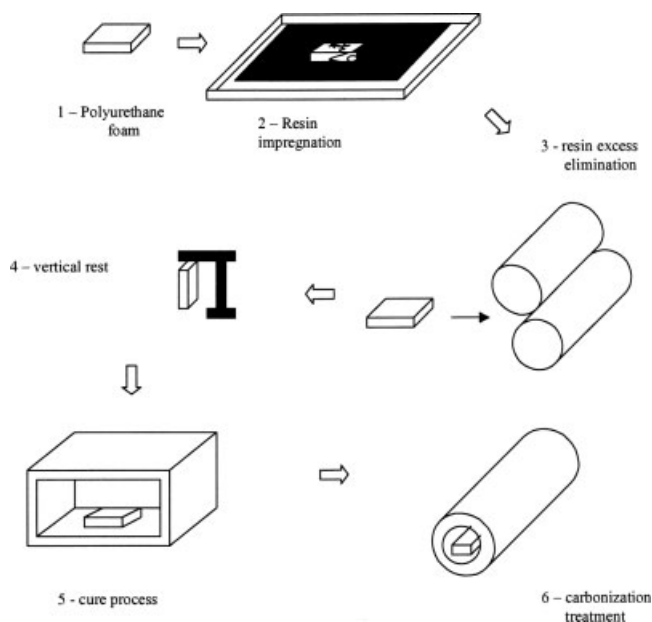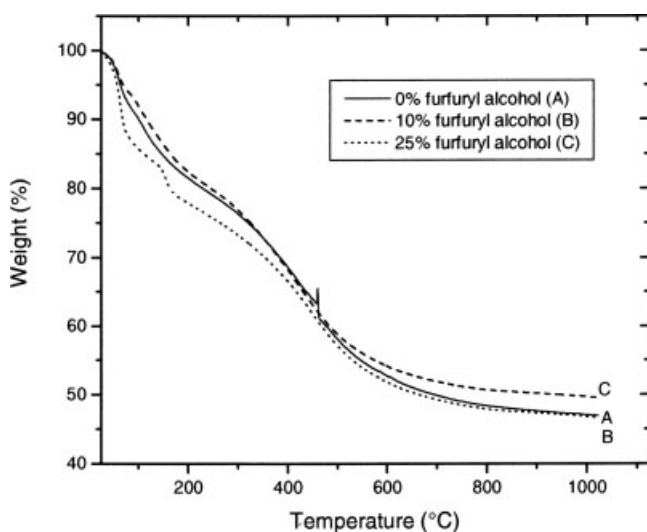
Figure 2 Impregnation process of polyurethane foam with furfuryl alcohol resin.

1130, according to an adaptation of the ASTM D1621-73, it was performed the compression tests.[28]

RESULTS AND DISCUSSION

Thermal analyses

One of the most important requisites in the raw material selection aiming the production of glassy carbon is the carbon yield.[2,3,5] Figure 3 and Table I show that the cured furfuryl alcohol resin samples, with and without furfuryl alcohol addition, present carbon yield after the heat treatment under inert

TABLE I
TG Results

| Temperature (°C) | Weight loss (%) | | | | | |
| | Furfuryl alcohol contents (%) | | | | | |
	0	5	10	15	20	25
100	10	8.0	7.0	15	11	14
170	17	15	14	20	18	20
260	21	22	20	25	23	25
280	23	23	21	26	24	26
300	25	25	23	28	26	28
380	30	30	28	33	30	32
460	35	37	36	40	37	39
800	52	50	49	52	51	52
1000	46	47	46	48	48	50
Residue	54	53	54	52	52	50

atmosphere between 46 and 50% (w/w). In this figure it is also observed that the weight loss behavior of all analyzed samples are similar.

As can be observed in Figure 3, there is no possible define different weight loss regions and the curve behavior can be attributed to the specimen degradation. Analyzing Table I, it can be observed that samples with furfuryl alcohol addition up to 10% present almost the same weight loss and the final residue. After this amount, the large quantity of free furfuryl alcohol trapped into the cured resin sample is eliminated as volatile, increasing the weight loss.

Figure 4 shows the thermal degradation mechanism of the furfuryl alcohol resin based on the literature.[5] Correlating the obtained TG results with the proposed degradation mechanism it is verified that the weight loss around 100°C is mainly attributed to the water loss. Above 170°C it is observed that the furan rings itself is broken evolving CO, CH_4, CO_2, and H_2O. This weight loss can be quantified as

Figure 3 Thermogravimetric analyses of furfuryl alcohol resin with 0, 10, and 25% of furfuryl alcohol contents.

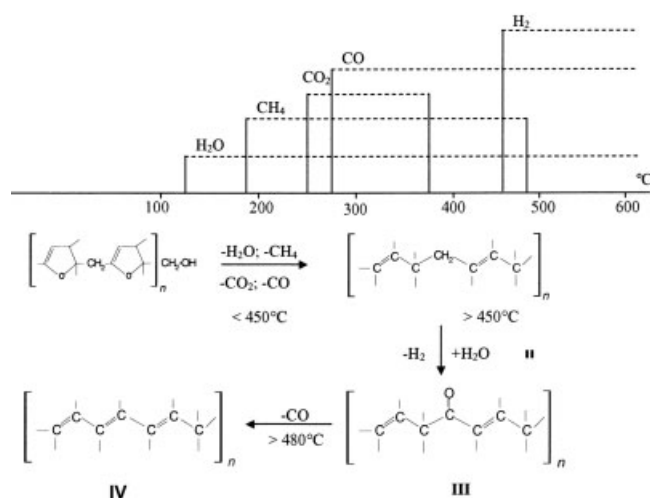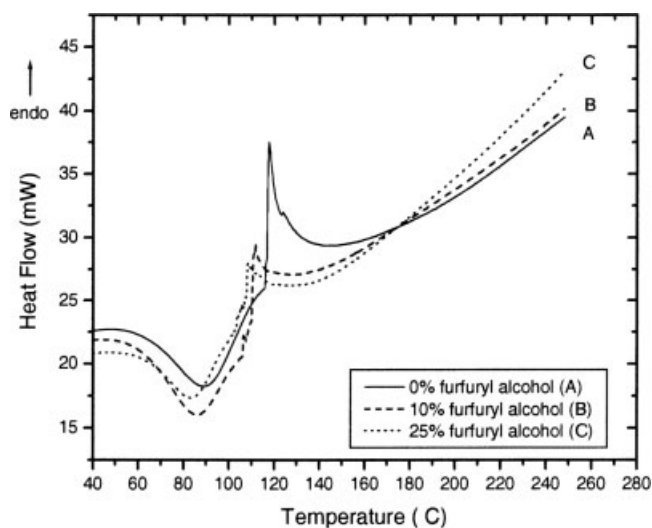**Figure 4** Thermal degradation mechanism of furfuryl alcohol resin.

Figure 5 DSC curves of furfuryl alcohol resin with 0, 10, and 25% of furfuryl alcohol.

observed in the TG analysis as shown in Figure 3. Around 450°C, it is proposed the methylene bridge oxidation by the H_2O presence, which leads to the polymer chain formation (III). During the heating, above 460°C, CO is evolved from the carbonyl bond, leading first to an unsaturated conjugated system (IV) and then to the carbon structure. In the end of this process residual carbon content can be observed.

DSC results of furfuryl alcohol resin (Fig. 5 and Table II) show that the initial polymerization temperature is located in the range of 50–60°C and the final temperature between 104 and 116°C for the analyzed samples. During the resin cure, water is eliminated as a by-product as mentioned in literature[5] and slightly showed in Figure 5 (see Fig. 5 near 100°C). The water is an undesirable by-product formed during the glassy carbon processing due to it favors the void presence into the cured resin and, consequently, into the glassy carbon. The voids contribute to the microcrack appearance, decreasing the final mechanical properties of the glassy carbon. These defects can be avoided by using an appropriate cure cycle of the resin.

The presence of water in the samples disguises the furfuryl alcohol volatilization, which makes the DSC technique not adequate to conclude about the better percentage of alcohol to be used in the furfuryl resin dilution.

The analysis of DSC curves shows that the cure reaction is more controlled between 60 and 80°C. Based on this range of temperatures it was performed the rheological analyses at 60, 70, and 80°C.

Correlating the thermal analysis results with the rheological parameters, it was possible to establish an adequate cure cycle of the furfuryl alcohol resin to be used in its cure, afterwards, in the glassy carbon manufacture.

Rheological analyses

Rheological analyses showed to be a very useful tool in the optimization of glassy carbon processing. The knowledge of the rheological characteristics of resin allows establishing an adequate cure cycle for its cure. The determination of the resin minimum viscosity value promotes a homogeneous impregnation of the substrate and an adequate glassy carbon manufacture looking for the end use.

The rheological analyses were performed aiming to determine the gelification time (gel time) using the relation of G′ (storage moduli) and G″ (loss moduli). Figure 6 presents the rheological parameters, storage moduli and loss moduli, of the furfuryl alcohol resin sample diluted with 10% of furfuryl alcohol, obtained at 60, 70, and 80°C. During the gel temperature, a three-dimensional infinite net coexists with numerous free chains.[24] After the thermoset resin system to reach the gel temperature, the net of polymeric chains densifies,[24] as a consequence of the cure reaction, which leads to the growing of the polymeric chains. The densification is associated with the ramification of the chain, as a function of the density of crossed connections, which decreases the flexibility and the mobility of the polymeric chains.

Before the gelification region (Fig. 6), the rheometric curves present Newtonian behavior, evidenced by the linearity of the storage and loss moduli values. This behavior is characteristic of thermoset resins because they present low molecular weight distribution.[24] As can be observed, the gelification region is reached in a shorter time period for the isotherms performed at 80°C, when compared with ones carried out at lower temperatures (60 and 70°C). This behavior is expected, because higher temperatures make the polymerization kinetics faster. Close to the gel time region a slighter growth of the storage modulus is verified when compared to the loss modulus, characterizing a viscoelastic behavior for the studied polymeric system.

The gel time values of the characterized resin samples (furfuryl alcohol resin diluted with 0, 5, 10, 15, 20, and 25% (w/w) of furfuryl alcohol) are depicted in Figure 7. It is observed that samples cured at

TABLE II
Initial and Final Cure Temperatures of Furfuryl Alcohol Resin

| Furfuryl alcohol (%)	Initial temperature (°C)	Final temperature (°C)
0	55	116
5	44	110
10	44	110
15	39	104
20	31	104
25	47	107
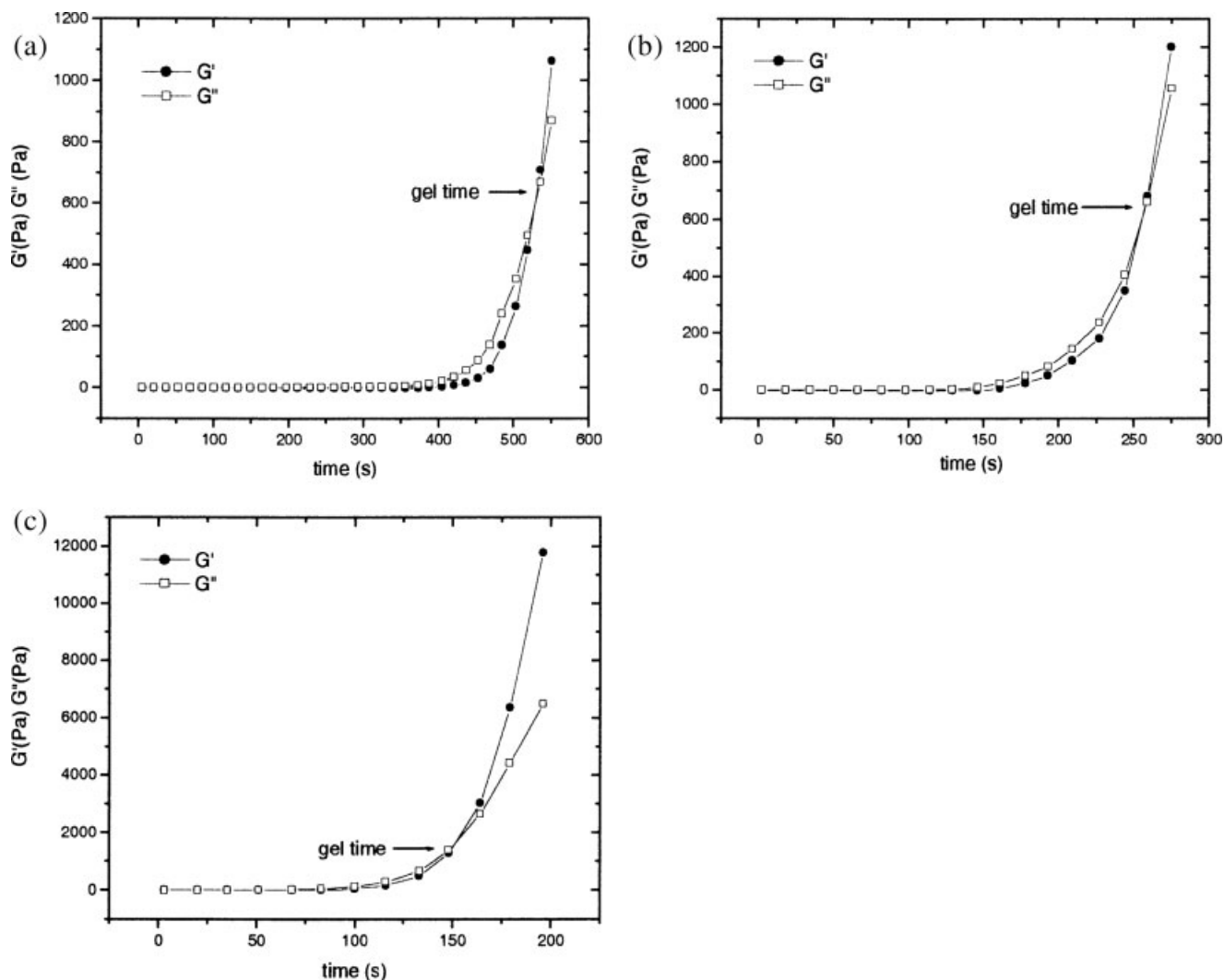
Figure 6 Isothermic rheograms of furfuryl alcohol resin added with 10% in furfuryl alcohol: (a) 60°C, (b) 70°C (c) 80°C.
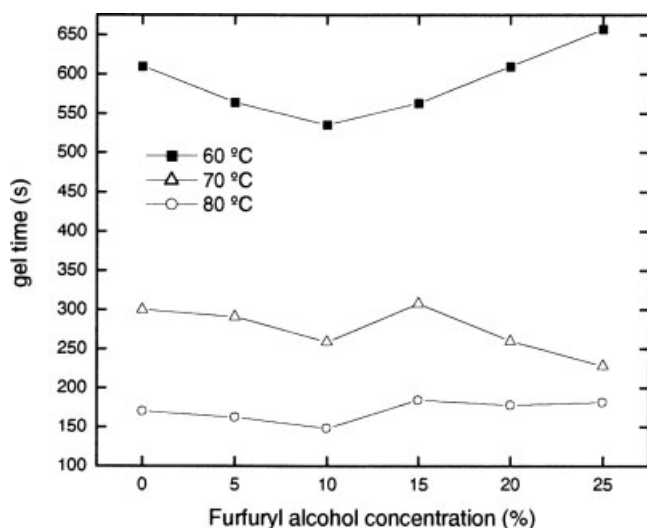
Figure 7 Gel time curves of furfuryl alcohol resin with different quantities of furfuryl alcohol. Analyses at 60, 70, and 80°C.

60°C showed the cure kinetics more adequate due to the gel time to occur in a longer time period (8–12 min). This parameters favors the volatile release, when compared with the cure carried out at 70 and 80°C (gel time lower than 6 min). This fact minimizes the occurrence of microcracks and voids during the carbonization heat treatment used in the glassy carbon manufacture.

Figure 8 shows the complex viscosity (η^*) behavior of the resin samples with different furfuryl alcohol contents. Figure 8(a) shows that samples diluted with 0, 5, 10, and 15% of furfuryl alcohol present almost the same time for the viscosity evolution (~ 450 s) when characterized at 60°C. However, concentrations above 20% shift the viscosity evolution time for values above 500 s. This behavior explains the observed cure kinetics where higher furfuryl alcohol contents in the samples decreases the cure rate (Fig. 7).
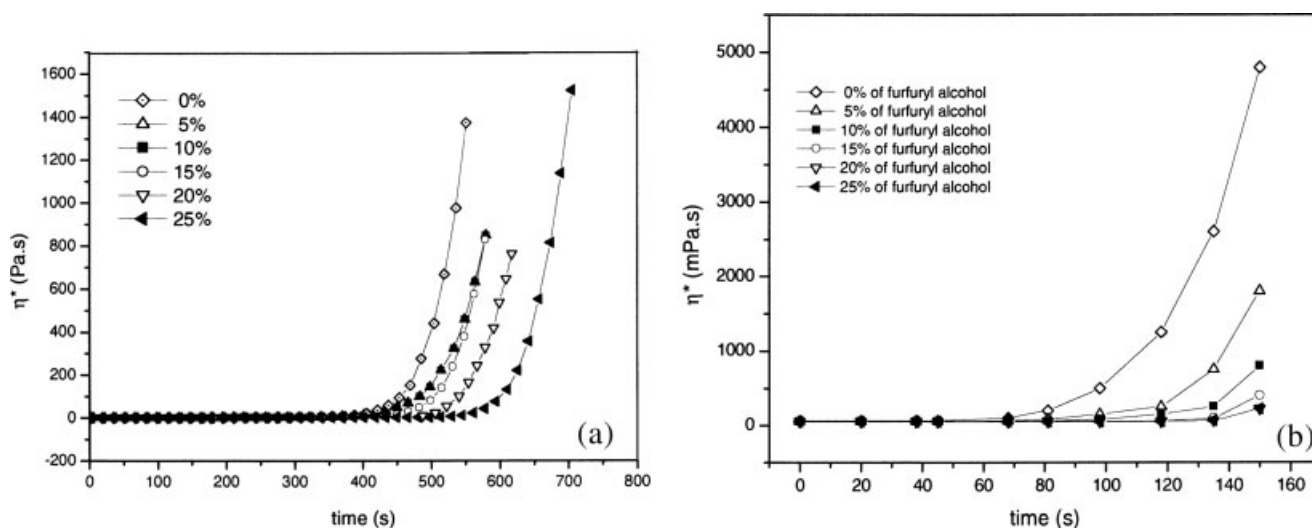
Figure 8 Complex viscosity curves of resin with different quantities of furfuryl alcohol, versus analysis time, at: (a) 60°C; (b) 80°C.

Figure 8(b) presents the furfuryl alcohol resin viscosity analyses performed at 80°C. It can be observed that samples diluted with 0, 5, and 10% of furfuryl alcohol present almost the same time period for the viscosity evolution (in the range of 120–140 s) and the samples with 15, 20, and 25% of alcohol present times for the viscosity evolution between 160 and 180 s. As expected, the viscosity decreases with the increase of temperature due to the gradual destruction of the van der Waals, polar and/or H-bond interactions.[24] Meanwhile, with the continuous increase of the time, the viscosity increases again. It happens due to the increase in the crosslink density caused by the increase of the polymerization rate of the thermoset resin. The faster the cure reaction occurs, more rapidly the resin viscosity increases. This behavior makes the release of trapped volatile matter into the resin more difficult. The volatile trapping leads to the porosity increase. Correlating these results it is possible to conclude that the more adequate temperature for the furfuryl resin processing is 60°C.
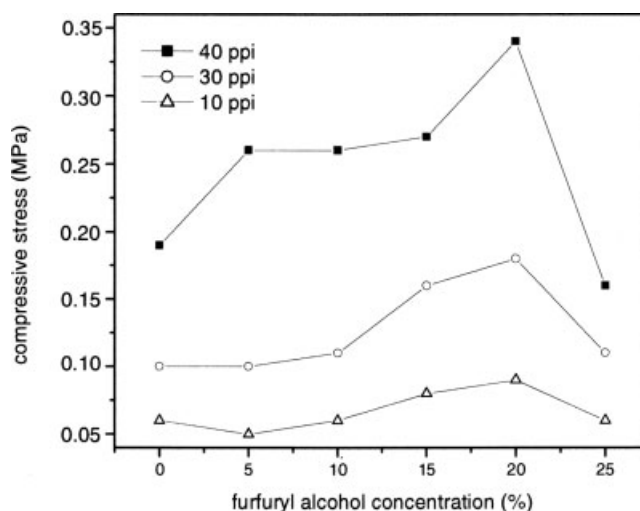
Compression tests

The Compression test is one of the most important tools to assess the mechanical behavior of foams.[2] Using this kind of test it is possible to select the appropriate material in order to be used as foam in the reticulated vitreous carbon manufacture.

Figure 9 depicts the results obtained by compression test of polyurethane foams impregnated with furfuryl alcohol resin. As can be observed, samples prepared with polyurethane foam with small pores (40 ppi), Type S, presented higher compression strength values when compared with the other pore sizes (Types I and L). This behavior is attributed to the samples with small pores that present a larger number of stems, consequently, a better tension distribution associate with the higher density values of the impregnated foams (Table III). Considering the same polyurethane foam type, samples impregnated with resin no diluted showed low compression strength values when compared with samples prepared with diluted resin, mainly for the foam Type S.

In Figure 9, it can be observed that all specimens increased the compression strength values with the furfuryl alcohol concentration up to 20% of furfuryl alcohol as solvent. This behavior is attributed to the dynamic viscosity decrease (from 16.8 mPa s to 4.3

Figure 9 Compression strength values of impregnated polyurethane foam with: S, Small pores (40 ppi); I, Intermediate pores (30 ppi); and L, Large pores (10 ppi).

TABLE III
Density and Average Pore Sizes of Impregnated Polyurethane Foam with Furfuryl Alcohol Resin Diluted with Different Furfuryl Alcohol Concentrations

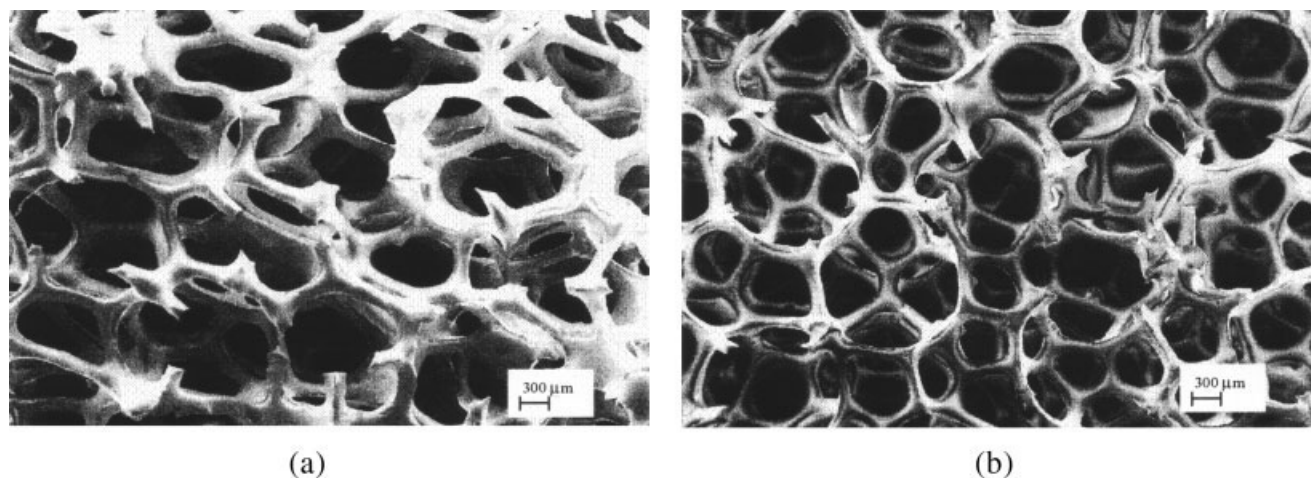| Furfuryl alcohol (%)	Polyurethane foam code	Pores size (μm)[a]	Density (g/cm³)	Dynamic viscosity (mPa s)
0	S (400–600 μm)	660	1.29	16.8
	I (600–900 μm)	900	1.29	
	L (900–1800 μm)	1148	1.25	
5	S	682	1.30	13.5
	I	939	1.29	
	L	1300	1.27	
10	S	684	1.26	11.4
	I	990	1.20	
	L	1452	1.17	
15	S	692	1.29	8.45
	I	1066	1.15	
	L	1762	1.19	
20	S	775	1.23	4.29
	I	1282	1.22	
	L	1893	1.19	
25	S	617	1.24	1.44
	I	986	1.19	
	L	1630	1.12	

[a] Evaluated by SEM analyses.

mPa s), which allows an easy resin flowing on the steams of foam during the impregnation step process, associated with a homogeneous mechanical anchorage. After 20% of furfuryl alcohol addition, happened a decrease of compression strength due to the very low viscosity (1.44 mPa s), that promotes a heterogeneous anchorage of the resin on the foam.

Scanning electron microscopy

SEM images reveal differences among the struts of the impregnated foams prepared with the different viscosity resin samples. Figure 10 is representative of the typical aspects observed in the cured samples and presents micrographs of polyurethane foam – Type S – impregnated with furfuryl alcohol resin. These images permit to estimate the pore sizes as the way to quantify the pore number per inch (ppi) of the impregnated foams. For example, pores with average diameter of 400–600 μm correspond to the code S (40 ppi) (Table III). This table shows that the medium porous size of the foam impregnated with furfuryl resin diluted with furfuryl alcohol is slightly higher than that one prepared with the resin without dilution. This tendency increases with the alcohol amount into the resin, up to 20% (w/w) of alcohol. These results suggest that the furfuryl alcohol attack the polyurethane foam promoting its swelling that increases, consequently, the medium diameter of the

(a)   (b)

Figure 10 Scanning electron microscopy of impregnated polyurethane foam with furfuryl alcohol resin: (a) without furfuryl alcohol addition; (b) with 10% of furfuryl alcohol.

transport pores. This observation did not degenerate the compression strength results, on the contrary these samples presented, generally, higher values (Fig. 9). The pore size determination is also important to estimate the density of the samples (Table III). Except to the fact that the foam samples with larger transport pores present lower density, no conclusive tendency is observed in this parameter related with the dynamic viscosity of the resin.

In a general way, it is also observed that the foams impregnated with resin without and with dilution present differences in the texture, as it is shown in Figure 10(a,b). Figure 10(a) presents struts thicker and heterogeneous, mainly in the strut crossing that shows regions richer in resin. Figure 10(b) shows that the sample impregnated with furfuryl resin diluted with 10% of furfuryl alcohol presents more uniform impregnation, with thinner struts when compared with that ones in Figure 10(a) (sample impregnated with the resin without dilution). This higher aspect ratio (length/wide ratio) is clear in the SEM image [Fig. 10(a)]. This aspect is obtained due to the lower resin viscosity (Table III) to favor its flow on the foam struts and the gel time to be reached faster when compared with the other diluted resin samples, avoiding that the resin flow out of foam.

This more homogeneous texture agrees with the compression results, where the impregnated foams with diluted resin present higher compression values (except for the samples diluted with 25% of furfuryl alcohol).

CONCLUSION

In this study, the best temperature was considered 60°C due to this temperature is near to the gel time temperature and also because this temperature promotes a slower cure kinetics, minimizing possible structural defects inside the cured material and, afterwards, in the vitreous carbon. The complex viscosity evolution confirmed the rheological results where the samples analyzed at 60°C presented the most adequate behavior, which favors a slower volatile release, which minimizes defects in the resin.

Furfuryl alcohol resin with 10% of furfuryl alcohol presented the best conditions to be used in the foam impregnation due to its high residual carbon (nearly 47%), intermediate viscosity values (11.4 Pa s), adequate gel time (8–12 min) for the impregnation step and good efficiency in the polyurethane foam impregnation (a homogeneous impregnation).

The mechanical resistance evaluation shows that furfuryl alcohol resin diluted with furfuryl alcohol presented increase in the resistance strength values when compared with the samples without dilution (as received). It is also verified that the foams with small pore sizes presented higher compression resistance when compared with that ones with larger pore sizes.

The correlation of the results shows that the resin viscosity used in the impregnation have a tight influence on the mechanical properties of cured samples and, consequently, in a further step, on the RVC manufacture.

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