

Synthesis and Characterization of Polyarylacetylene for Use in the Monolithic Vitreous Carbon Processing

Silvia Sizuka Oishi, Edson Cocchieri Botelho

Faculdade de Engenharia de Guaratinguetá, Universidade Estadual Paulista – UNESP, Guaratinguetá, SP

Christine Keiko Luscombe

Department of Materials Science and Engineering, University of Washington, Seattle/WA, United States

Mirabel Cerqueira Rezende

Instituto de Ciência e Tecnologia – ICT, Universidade Federal de São Paulo – UNIFESP, São José dos Campos, SP

Abstract: In this work, polyarylacetylene (PAA) prepolymer obtained from 1,4-diethynylbenzene was evaluated as polymeric precursor of monolithic vitreous carbon (MVC). The monomer 1,4-diethynylbenzene was synthesized and the PAA prepolymer was prepared with 13, 16 and 19 wt % of nickel catalyst. The best percentage of nickel catalyst considered was 13 wt %, due to the lower molecular weight and polydispersity index and higher carbon yield. The traditional production of MVC is obtained from phenolic and poly(furfuryl alcohol) resins, which require many hours to pyrolyze due to the large quantity of gases generated. Furthermore, the porosity is hard to control using these conventional resins. Polyarylacetylene releases little volatiles due to the polyaddition reaction and the aromatic rings in PAA chain also provide a high thermal stability, therefore the heat treatment could be faster without cracking the carbon material. This would also lower the cost of fabrication of MVC, in addition to the low porosity observed, making this polymer a good matrix for MVC.

Keywords: Polyarylacetylene, 1,4-diethynylbenzene, monolithic vitreous carbon, porosity.

Introduction

Polyarylacetylene (PAA) is a high temperature polymer, obtained from nonpolar ethynyl and aromatic hydrocarbons such as *m*-diethynylbenzene and *p*-diethynylbenzene, which after cure presents only carbon and hydrogen atoms and a high crosslinking structure^[1,2]. PAA development began in the 60s, during the search for thermally stable polymers aiming to satisfy the needs of the aerospace industry to be used as ablative insulator for rocket motors and polymeric raw material for carbon-carbon composite processing^[1,3-6]. PAA was first synthesized by Hay^[7], using the same oxidative coupling of acetylenes methodology. Since then, PAA has been synthesized using thermal, irradiation, electroinitiated and catalytic polymerization methods^[8-11].

The synthesis routes most used involve the polycyclotrimerization and thermal reaction of diethynylbenzene for an oligomer or a prepolymer preparation, that reduces substantially the heat of reaction decreasing the exotherm during processing^[5,12]. The cyclotrimerization is usually a nickel-catalyzed reaction in which three ethynyl groups are mostly linked together to form a benzene ring, as presented in Figure 1^[13-15]. The cyclotrimerization produces aromatic rings stabilized by resonance that improve the thermal

stability of the system and increase the carbon yield during pyrolysis^[14,16,17].

Some features that make PAA the best alternative as carbonaceous materials precursor in relation to conventional thermoset resins are: cure by addition instead by condensation reaction; high char yield at 1000 °C in nitrogen (~80%); lower shrinkage during pyrolysis and lower moisture absorption. Among the shortcomings of PAA are: the exothermic cure; the polymer is brittle and with low structural integrity due to highly crosslinked network structure and the high cost compared to phenolic and poly(furfuryl alcohol) resins^[6,18,19]. Due to the disadvantages present by PAA more attention has been given in obtaining a modified resin to overcome the problems with processing and mechanical properties mainly in composites^[2,18-23].

In this work, PAA was studied as precursor matrix of monolithic vitreous carbon (MVC), which is characterized by the presence of micro and mesopores. All carbonaceous materials contain pores, except highly oriented pyrolytic graphite, thus, by controlling both the processing parameters and the raw materials, it is possible to control the porosity^[24-27]. The presence of pores in MVC has a significant effect on many important features, such as, density, surface area, mechanical strength and elastic

Corresponding author: Edson Cocchieri Botelho, Departamento de Materiais e Tecnologia, Faculdade de Engenharia de Guaratinguetá – FEG, Universidade Estadual Paulista – UNESP, Av. Ariberto Pereira da Cunha, 333, Pedregulho, CEP 12516-410, Guaratinguetá, SP, Brasil, e-mail: ebotelho@feg.unesp.br

modulus^[28,29]. The porosity caused by conventional resins restricts the applicability of MVC in potential areas such as aerospace and medical. Therefore, the possibility to attend specific requirements for such applications, makes the high cost of PAA advantageous with regard to the final properties achieved.

In order to minimize the final cost of PAA, the monomer 1,4-diethynylbenzene (1,4-DEB) was synthesized using low cost starting material and the PAA prepolymer was obtained by using different percentages of nickel catalyst. The literature available and consulted describes few results involving the characterization of MVC obtained from PAA^[30,31]. In this way, the MVC was processed using PAA powder and analyzed by scanning electron microscopy (SEM).

Experimental

Materials

The following chemicals and solvents were used as received: carbon tetrachloride (Sigma-Aldrich, 99.9%), divinylbenzene (Alfa Aesar, mixture of isomers 80%), bromine (Sigma-Aldrich, 99.5%), nickel(II) acetylacetonate (Alfa Aesar), triphenylphosphine (Tokyo Chemical Industry, 98.0%), sodium sulfite (JTBaker), hexane (EMD, 98.5%), methanol (EMD, 99.8%), potassium hydroxide (EMD, 85.0%), N,N-dimethylformamide (JTBaker, 99.8%), anhydrous benzene (Alfa Aesar, 99.8%).

Synthesis of 1,4-diethynylbenzene monomer

1,4-Diethynylbenzene (1,4-DEB) was synthesized based on a patent from Yongjia et al.^[32]. Carbon tetrachloride (12.5 mL) and divinylbenzene (5.0 g) were placed in a 250 mL three-necked flask. An addition funnel was charged with bromine (25 mL) and bromine was added dropwise. The reaction was held under dark with nitrogen flow. A solution of sodium sulfite (5% w/v) was placed in the gas output to neutralize the hydrobromic acid and volatilized bromine. After completed the bromine addition, the reaction was kept under stirring for about 90 min. Then a large amount of white precipitate (1,4-bis(1,2-dibromoethyl)benzene) was formed. Thin layer chromatography (TLC) showed the reaction was finished.

The solution was filtered and the white precipitated was dehydrobrominated. The filtrate solution is a mixture of 1,3-bis(1,2-dibromoethyl)benzene and 1,4-bis(1,2-dibromoethyl)benzene, so only the white precipitated was used to get the pure 1,4-DEB monomer. For dehydrobromination step, potassium hydroxide (3.75 g) was added slowly to methanol (12.5 mL) until it became totally soluble. Then about 3 g (obtained amount) of 1,4-dibromo-vinylbenzene was added to the flask. The mixture was heated to reflux (80 °C) for 2 h with nitrogen, so a white precipitated (KBr) was formed and TLC showed the reaction was finished. The KBr was removed by filtration and the filtrate was cooled in ice bath and a pale yellow solid is formed. This yellow solid (1,4-DEB) was removed by filtration and washed with cold deionized water. After

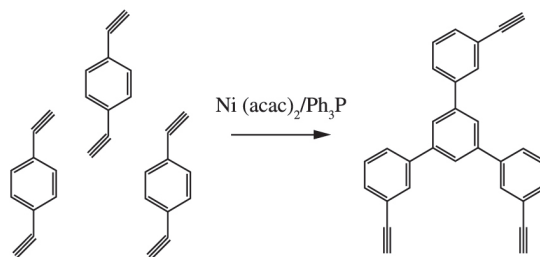


Figure 1. Cyclotrimerization reaction of 1,4-diethynylbenzene^[13-15].

the monomer was dried in a desiccator, it was purified by sublimation.

Preparation of PAA prepolymer

PAA prepolymer was prepared using nickel catalyst according to a procedure previously reported^[12,17]. The polymerization reaction was carried out using percentages of nickel catalyst varying from 13 to 19 wt% and reaction times varying from 1 h to 5 h.

Monolithic vitreous carbon sample preparation

The prepolymer was obtained as a powder and compressed in a circular die with 12.7 mm diameter using a hydraulic press. A pressure about 5000 psi was used to compress 0.25 g of PAA powder. The PAA with disc shapes were heat treated under nitrogen flow, from room temperature until 1000 °C, in a tube furnace using a heating rate of 1 °C/min, remaining 1 h in the final temperature.

Characterization

The 1,4-DEB and PAA prepolymer was characterized by proton nuclear magnetic resonance (¹H NMR) using a Bruker Avance AV-300 or AV-500 and deuterated chloroform as solvent. Fourier transform infrared spectroscopy (FT-IR) measurements were performed using a Bruker Vertex 70 instrument, configured with a diamond ATR sampling interface. The FT-IR spectra were collected in the mid-infrared region (4000 cm⁻¹ to 400 cm⁻¹), from 50 scans with 4 cm⁻¹ resolution. Molecular weights of the PAA prepolymers were obtained using a Viscotek TDA 305 gel permeation chromatography (GPC) and polystyrenes GPC standards in tetrahydrofuran (THF) as reference. For GPC analyses, about 1 mg of PAA prepolymer sample was dissolved in 1 mL of THF. Differential scanning calorimetry (DSC) analyses were performed on a TA instruments Q20, at a heating rate of 10 °C/min, temperature scan from 30 to 350 °C, under nitrogen flow of 50 mL/min. About 2 mg of sample was used and a non-hermetic sample holder. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA 7 under constant nitrogen flow (40 mL/min), temperature scan from 30 to 1000 °C, at a heating rate of 10 °C/min and 4 mg sample mass. The morphological characteristics of PAA prepolymer and MVC discs surfaces and fractured surfaces were analyzed by scanning electron microscopy using a Jeol JSM 7000F and a Zeiss EVO LS-15 equipment, respectively.

Results and Discussion

Characterization of 1,4-DEB monomer

The ^1H NMR spectra presented in Figure 2 confirms the 1,4-DEB obtaining due to the proton signals at $\delta = 7.44$ ppm (s, 4H, aromatic protons) and $\delta = 3.17$ ppm (s, 2H, $\equiv\text{C-H}$). Figure 3 present FT-IR spectra of 1,4 DEB that confirms the results from ^1H NMR with the presence of characteristic band of acetylene triple bonds at 3267 cm^{-1} and 2101 cm^{-1} . The band at 827 cm^{-1} is related to the benzene ring p-disubstituted.

The TGA thermogram for 1,4-DEB is shown in Figure 4. The high volatility of the monomer can be observed around $100\text{ }^\circ\text{C}$, with weight loss of almost 80%. This temperature coincides with the monomer melting point and shows that before expose to a high temperature, the monomers need crosslink to prevent its vaporization. This behavior highlights the necessity to work with the prepolymer for release partially the heat of reaction and to prevent monomers loss because of the high volatility.

Characterization of PAA prepolymer

Figure 5 shows the ^1H NMR spectrum of PAA prepolymer with 13 wt% of nickel catalyst that confirms the polymer's achievement due to the presence of resonance peaks at 7.1-7.8 ppm assigned to the protons attached to the aromatic rings and the peaks at 3.1-3.3 ppm are assigned to the protons of acetylene ($\equiv\text{C-H}$). Although the major reaction is through cyclotrimerization, there are undesired peaks around 1.3 and 2.1 ppm resulted from linear or branched free-radical polymerization^[12].

The effect of different percentages of nickel catalyst and reaction times on reaction yield and molecular weight are shown in Table 1.

The percentage of nickel catalyst and the reaction times were adjusted to obtain a good yield, without reaching the gelation during polymerization. Increasing the percentage

of catalyst, the reaction time decrease and the yield can reach 77.2% using 19 wt% of nickel catalyst. The molecular weight is just an estimate since the GPC standards is a linear polymer, while PAA is a branched polymer. Moreover, the prepolymer catalyzed with 19% of nickel was partially soluble in THF. Based on the reaction time and yield, it was chosen to work with prepolymers catalyzed with 13, 16 and 19 wt% of nickel catalyst that presented more than 70% yield.

Figure 6 shows DSC curves for the prepolymers 13%Ni 3h30, 16%Ni 2h30 and 19%Ni 2h. The nomenclatures of different PAA prepolymers are formed by the percentage of nickel catalyst and the reaction time. The PAA 19%Ni 2h presents two exothermic peaks related to a broad molecular weight distribution. The PAA 13%Ni 3h30 does not show this behavior and 16% of nickel catalyst there is just a slight shoulder. Therefore, the PAA 13%Ni shows the lowest PDI in contrast to the result presented by GPC. This effect can be explained by the full sample portion used during DSC analyses while insoluble portion cannot be analyzed by GPC.

Table 2 shows the onset, peak, endset temperatures and enthalpy change of the polymers analyzed. Due to the broad molecular weight distribution presented by the PAA 19%Ni 2h, this polymer also has a broader range of cure. The larger enthalpy change value is related to greater amount of residual acetylene groups, so in this case the PAA with 13%Ni 3h30 has the greatest amount of these groups.

Thermogravimetric analysis is essential in determining the applicability of PAA as vitreous carbon precursor. The TGA curves and the carbon yield at $1000\text{ }^\circ\text{C}$ are presented in Figure 7. The three PAA prepolymers analyzed present an initial loss mass between 50 to $130\text{ }^\circ\text{C}$ that can be related to the volatilization of oligomers with low molecular weight. The higher carbon yield and thermal stability presented by the sample 13%Ni 3h30 can be assigned to the presence of

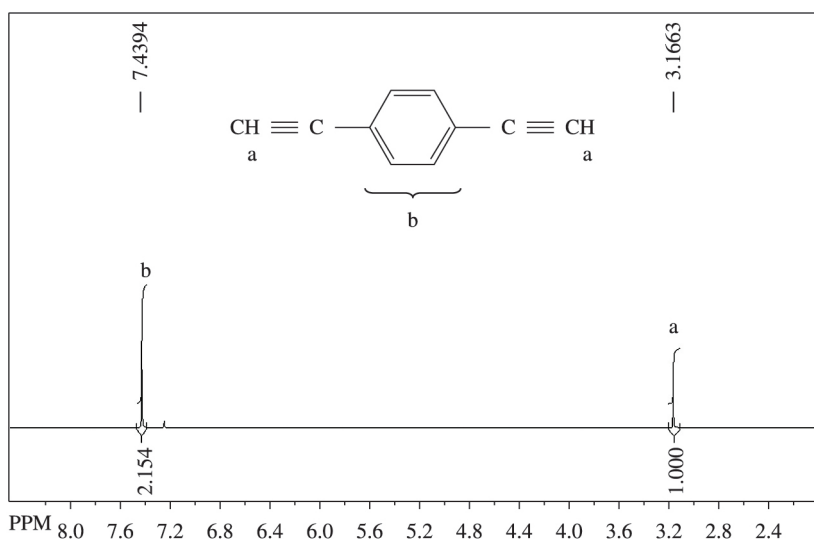


Figure 2. ^1H NMR spectrum of 1,4-DEB monomer.

residual acetylene groups in larger amount, as confirmed by DSC analysis.

The PAA prepolymers were compressed in a press using a circular die. Figure 8 shows the representative micrographs of each prepolymer disk surface and fractured cross section at the same magnification of 10,000X. The prepolymer 19%Ni 2h presents a better compacting surface, probably, due to the broad molecular weight that promotes

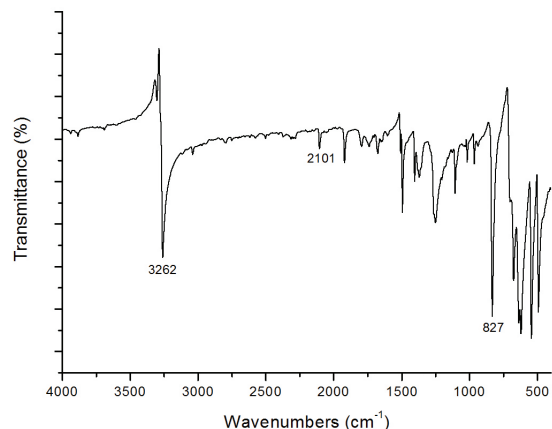


Figure 3. FT-IR spectrum of 1,4-DEB monomer.

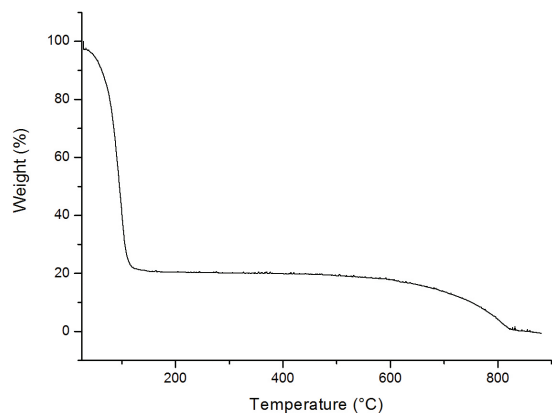


Figure 4. TGA curve of 1,4-DEB monomer.

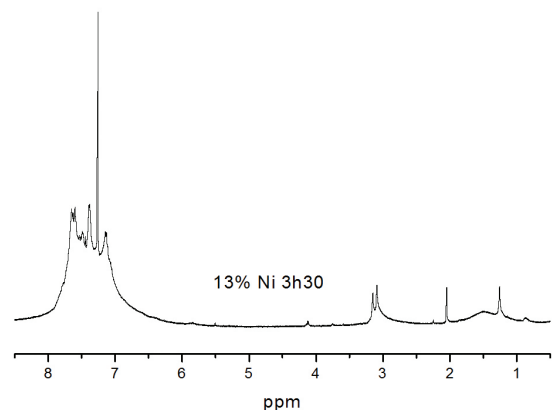


Figure 5. ¹H NMR Spectrum of PAA prepolymer with 13 wt% of Ni catalyst.

a better structure packing. The prepolymer surfaces with 13% and 16% of nickel catalyst present more irregular agglomerations, pores and roughness. Whereas the 16% and 19% of Ni samples cross section show large chunks, differently, the 13% of Ni sample cross section seems to be smoother probably due to the lower molecular weight.

Table 1. Polymerization conditions, yield of reaction, the number average molecular weight (Mn) and polydispersity index (PDI) of PAA prepolymers.

PAA	Reaction time	Yield (%)	Mn (g/mol)	PDI
10%Ni	5h	52.8%	1044	3.6
13%Ni	2h30min	42.0%	1118	2.7
13%Ni	3h30min	70.7%	1065	3.8
16%Ni	2h30min	72.6%	1155	3.0
19%Ni	1h	42.0%	1260	2.4
19%Ni	2h	77.2%	1217	2.3

Table 2. Results of onset, peak, endset temperatures and enthalpy change.

PAA	T _{onset} (°C)	T _{pico} (°C)	T _{endset} (°C)	ΔH (J/g)
13%Ni 3h30	133.2	202.5	280.8	297.5
16%Ni 2h30	128.1	214.0	282.8	274.7
19%Ni 2h	117.0	205.8	296.2	213.9

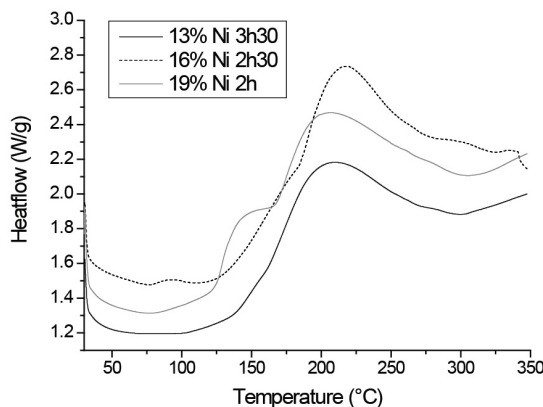


Figure 6. DSC curves for PAA with 13%Ni 3h30, 16%Ni 2h30 and 19%Ni 2h.

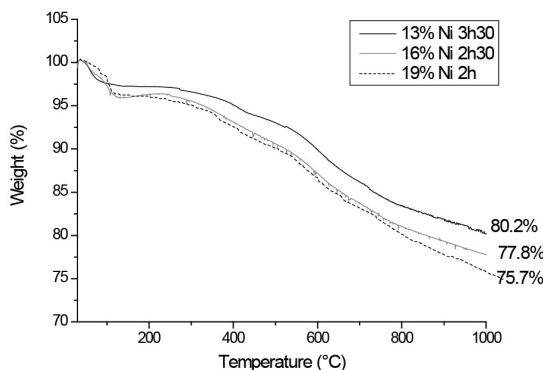


Figure 7. TGA curves for PAA with 13%Ni 3h30, 16%Ni 2h30 and 19%Ni 2h.

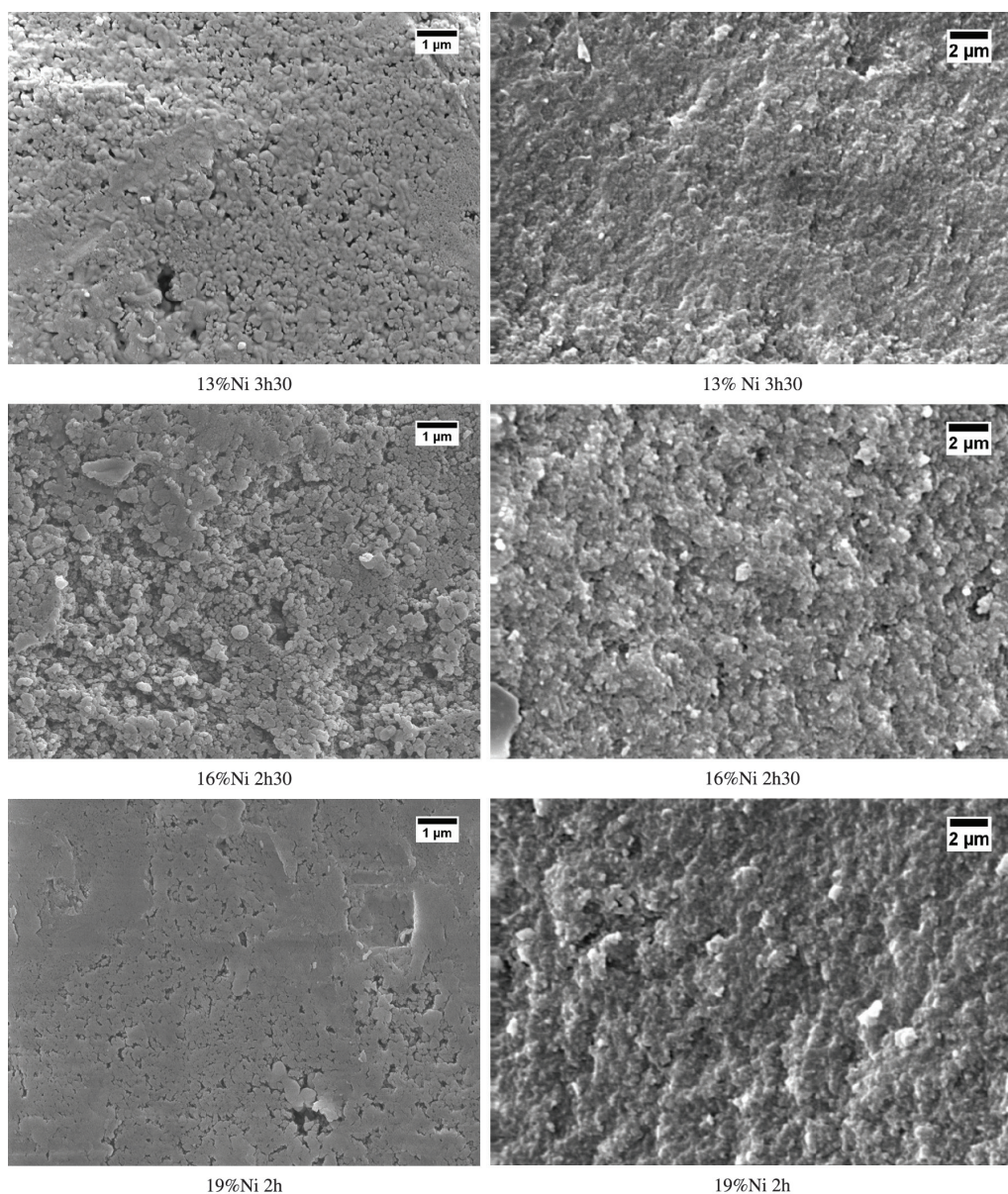


Figure 8. SEM of compressed PAA prepolymers surfaces (left column) and fractured cross section (right column).

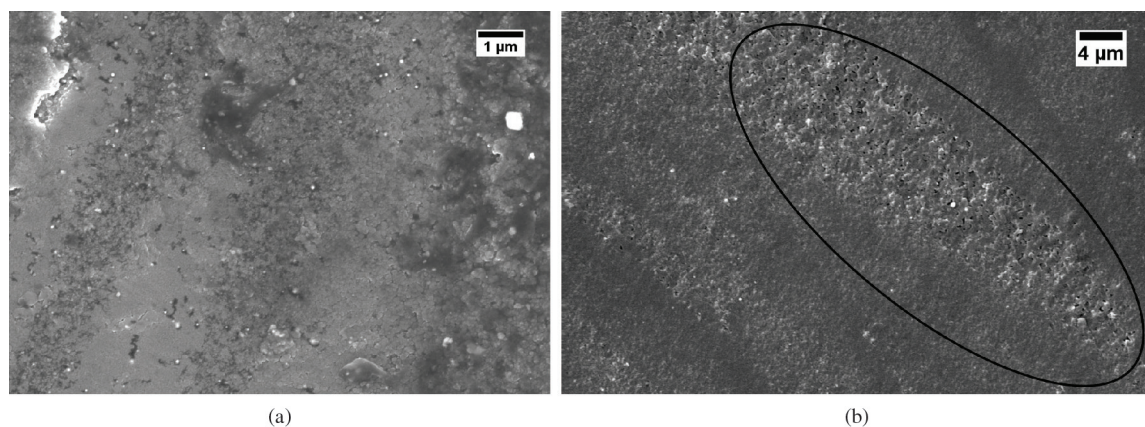


Figure 9. SEM images of heat treated PAA at 1000 °C: (a) surface and (b) fractured cross section.

Although the PAA with 19% of nickel catalyst has shown a better structure packing, the polymer with 13% of nickel catalyst was chosen to be heat treated due to the higher carbon yield, lower molecular weight and lower PDI as shown by TGA, GPC and DSC analyses. Figure 9 shows a representative surface and fractured cross section morphology of the PAA 13%Ni 3h30 heat treated until 1000 °C.

After heat treatment until 1000 °C, it can be observed the surface is smoother and more compacted. This result can be explained by the material contraction during carbonization and the flexibility of the precursor polymeric chains allowing a better accommodation. The resulting material shows a reduction about 8% in its diameter. Some small porosity with pores around 0.1 µm, can be noticed on the sample cross section as highlighted and could have been originated due to the bad compaction of the PAA powder.

Conclusions

The PAA prepolymer prepared with 13, 16 and 19 wt% of nickel catalyst reached the best yield (above 70%) and presented short reactions. The PAA with 13 wt% of nickel catalyst was chosen as the best condition to be heat treated due to the lower molecular weight and polydispersity index and higher carbon yield. The use of PAA allowed the carbonization at a heating rate of 1 °C/min, which provides a great economy of time and lower energy costs compared to conventional resins. The MVC processed from prepolymer with 13 wt% of nickel catalyst presented a low porosity, making the PAA a good matrix for this purpose.

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References

- Hergenrother, P. M. - High Perform. Polym., **15**, p.3 (2003).
- Wang, S.; Li, M.; Gu, Y. & Zhang, Z. - J. Compos. Mater., **44**, p.3017 (2010). <http://dx.doi.org/10.1177/0021998310371539>
- Economy, J.; Jung, H. & Gogeva, T. - Carbon, **30**, p.81 (1992). [http://dx.doi.org/10.1016/0008-6223\(92\)90110-1](http://dx.doi.org/10.1016/0008-6223(92)90110-1)
- Rellick, G. - "Carbon and graphite matrices in carbon-carbon composites: an overview of their formation, structures and properties", US Patent No A683852 (1992).
- Zaldivar, R. J.; Kobayashi, R. W.; Rellick, G. S. & Yang, J. M. - Carbon, **29**, p.1145 (1991). [http://dx.doi.org/10.1016/0008-6223\(91\)90032-E](http://dx.doi.org/10.1016/0008-6223(91)90032-E)
- Njuguna, J.; Pielichowski, K. & Desai, S. - Polym. Adv. Technol., **19**, p.947 (2008). <http://dx.doi.org/10.1002/pat.1074>
- Hay, A. S. - J. Org. Chem., **25**, p.1275 (1960). <http://dx.doi.org/10.1021/jo01077a633>
- Cherkashin, M. I.; Kisilitsa, P. P. & Berlin, A. A. - B. Acad. Sci. USSR Ch+, **16**, p.2335 (1967). <http://dx.doi.org/10.1007/BF00911839>
- Kobayashi, E.; Ohashi, T. & Furukawa, J. - Makromol. Chem., **187**, p.2525 (1986). <http://dx.doi.org/10.1002/macp.1986.021871102>
- Zhan, X. & Yang, M. - Eur. Polym. J., **37**, p.1649 (2001). [http://dx.doi.org/10.1016/S0014-3057\(01\)00016-7](http://dx.doi.org/10.1016/S0014-3057(01)00016-7)
- Grovu-Ivanoiu, M.; Bulacovschi, V. & Simionescu, C. I. - Makromol. Chem., **186**, p.2247 (1985). <http://dx.doi.org/10.1002/macp.1985.021861105>
- Tseng, W. C.; Chen, Y. & Chang, G. W. - Polym. Degrad. Stab., **94**, p.2149 (2009). <http://dx.doi.org/10.1016/j.polymdegradstab.2009.09.008>
- Chalk, A. J. & Gilbert, A. R. - J. Polym. Sci. Part A Polym. Chem., **10**, p.2033 (1972).
- Korshak, V. V. - Pure Appl. Chem., **39**, p.65, (1974).
- Hergenrother, P. M. - J. Macromol. Sci. Rev. Macromol. Chem., **19**, p.1 (1980). <http://dx.doi.org/10.1080/00222358008081045>
- Swanson, S.A.; Fleming, W. W. & Hofer, D. C. - Macromolecules, **25**, p.582 (1992). <http://dx.doi.org/10.1021/ma00028a015>
- Katzman, H. A.; Mallon, J. J. & Barry, W. T. - J. Adv. Mater., **26**, p.21 (1994).
- Fu, H. J.; Huang, Y. D. & Liu, L. - Mater. Sci. Technol., **20**, p.1655 (2004). <http://dx.doi.org/10.1179/026708304225022188>
- Qi, H.; Pan, G.; Yin, L.; Zhuang, Y.; Huang, F. & Du, L. - J. Appl. Polym. Sci., **114**, p.3026 (2009). <http://dx.doi.org/10.1002/app.30946>
- Wang, M. C. & Zhao, T. - J. Appl. Polym. Sci., **105**, p.2939 (2007). <http://dx.doi.org/10.1002/app.26465>
- Xu, K.; Peng, H. & Tang, B. Z. - Polym. Prepr., **42**, p.555 (2001).
- Yang, M.; Shi, S.; Wang, M.; Luo, Z.; Qiu, W.; Wang, Y.; Feng, Z. & Zhao, T. - Polym. Adv. Technol., **22**, p.1471 (2011). <http://dx.doi.org/10.1002/pat.16323>.
- Luo, Z.; Yang, M.; Wang, M. & Zhao, T. - High Perform. Polym., **23**, p.575 (2011). <http://dx.doi.org/10.1177/0954008311421832>
- Sastri, S. B.; Armistead, J. P. & Keller, T. M. - Carbon, **31**, p.617 (1993). [http://dx.doi.org/10.1016/0008-6223\(93\)90116-R](http://dx.doi.org/10.1016/0008-6223(93)90116-R)
- Botelho, E. C.; Scherbakoff, N. & Rezende, M. C. - Carbon, **39**, p.45 (2001).
- Ferrari, P. E. & Rezende, M. C. - Polímeros, **8**, p.22 (1998). <http://dx.doi.org/10.1590/S0104-14281998000400005>
- Oishi, S. S.; Rezende, M. C.; Origo, F. D.; Damião, A. J. & Botelho, E. C. - J. Appl. Polym. Sci., **128**, p.1680 (2013).
- Nishikawa, K.; Fukuyama, K. & Nishizawa, T. - Jpn J Appl Phys., **37**, p.6486 (1998). <http://dx.doi.org/10.1143/JJAP.37.6486>
- Oishi, S. S.; Botelho, E. C.; Paula, C. C. & Rezende, M. C. - J. Adv. Mater., **42**, p.62 (2010).
- Callstrom, M. R.; Neenan, T. X.; McCreery, R. L. & Alsmeyer, D. C. - J. Am. Chem. Soc., **112**, p.4954 (1990). <http://dx.doi.org/10.1021/ja00168a049>
- Stephens, E. B. & Tour, J. M. - Macromolecules, **26**, p.2420 (1993). <http://dx.doi.org/10.1021/ma00062a005>
- Yongjia, S.; Jinfeng, X.; Farong, H.; Lianfa, Y. - "Preparation of 1,4-diethynylbenzene", CN Patent 1680228 (2005).

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