BULETINUL Universității Petrol – Gaze din Ploiești	Vol. LX No. 2/2008	131-136	Seria Matematică - Informatică - Fizică

Microcellular Carbon from Polymer Materials Pyrolysis

Georgeta Nan*, Ioan Stamatin**, Adriana Andronie**, Ştefan Iordache**, Nicolae Moşescu*, Şerban Stamatin**, Marilena Ceauş**

* Universitatea Petrol-Gaze din Ploieşti, Bd. Bucureşti 39, Ploieşti
e-mail: n_georgeta@yahoo.com

** Universitatea din Bucureşti, Facultatea de Fizică, Centrul de Cercetare 3Nano-SAE

Abstract

The microcellular carbon is an advanced material due to its properties related to chemical inertness and thermal conductivity where high rate of heat exchange is required. In addition the carbon resulted from polymer pyrolysis exhibit various properties of gas adsorption and separation. Microcellular carbon is usual obtaining by foaming of the pyrolized polymers with different agents. The results lead to uncontrolled pore sizes. This contribution deals with a new method of the polymer pyrolysis consisting of thermal treatment of the composite materials polymer-nondecomposable salts. At 700^{0}C structures of microcellular carbon have been developed from polyacrylonitrile polymer matrices with addition of salt. The structure and the properties of polymer materials were investigated by, Raman and SEM.

Key words: microcellular, carbon, pyrolysis

Introduction

Microcellular Carbon (CMC) and glassy reticulate carbon (RVC) are advanced materials known for its mechanical resistance and high porosity, biocompatibility and respectively by thermal and electrical conductivity depending on the temperature of heat treatment. The difference between the CMC and RVC lies in the method of pyrolysis of precursor materials and heat treatment. RVC results from the pyrolysis of organic compounds in the presence of foaming agents. CMC results from pyrolysis of polymeric matrixes combined with materials which do not decompose at high temperatures heat.

The additional material is extracted by the chemical dissolution, resulting a foaming microcellular structure which pores size is depending on the size of the used powder. Their properties have been extensively studied in the past decades in many applications such as: coatings for thermal protection of spatial vehicles [1, 2], prostheses to bone [3], for heart valves [4-6], molecular sieves [7], support for catalysts [8].

Electrical conductivity and the conduction mechanisms are determining parameters for the use of CMC's as electrodes in many electrochemical applications like bears for electrode-membrane assemblings in mini combustion piles.. Electrical conductivity and electrochemical activity of the carbonic structures depends on the carbohydrates polyaromatic crystals resulting from pyrolysis and are semiconductors with intrinsic values between 102-1010 Ωcm.

RVC shows a decrease in electrical resistivity depending on the temperature of heat treatment and on the nature of the precursor. In the case of CMC's the interim phase induces an organization restriction of polyaromatic structures in grafens at the interface of the granules of the added material. In the case of this contribution is studied the pyrolysis and conversion of the polyacriylonitrile mixed with powder of sodium chloride. The microstructure and composition resulting from the heat treatment was studied by SEM and Raman.

Experimental Details

Materials: Polyacrylonitrile and sodium chloride, technical powders of indigenous origin.

Preparation: Dust are mixed in gravimetric proportion of 10% NaCl, combined and pressed to 6 tf in a matrix with a diameter of 30mm, on tablets of 0,3-0,5 mm thickness.

Pyrolysis PAN with 10% NaCl was made to the temperature of 700^{0}C. Oven (model-L200M company Caloris) where the process of pyrolysis is done is electrically powered and is equipped with a built-in-thermocouple which allows measurement of internal temperature (fig. 1).

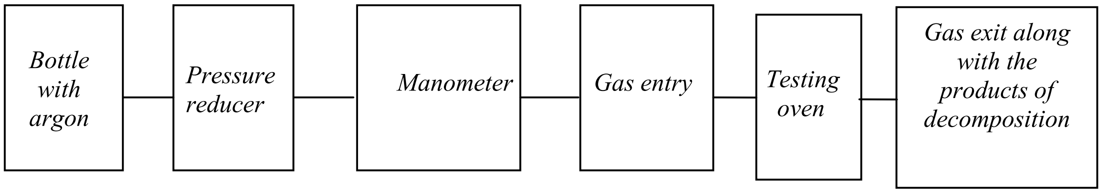


Fig. 1. Scheme of experimental device

The obtained tablets (set A and set B) been put under the same heat treatment (fig. 2).

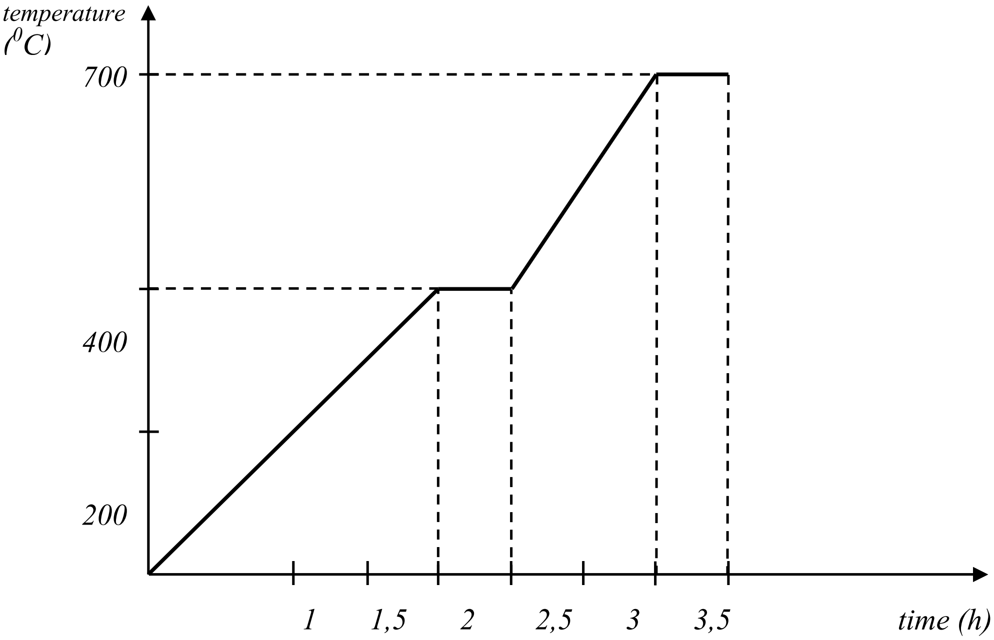


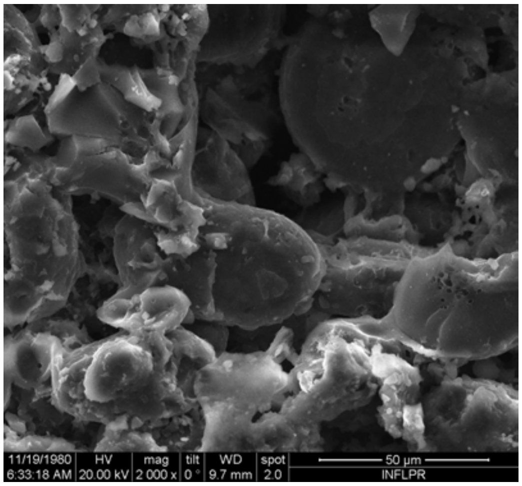
Fig. 2. Chart time-temperature of the pyrolysis process

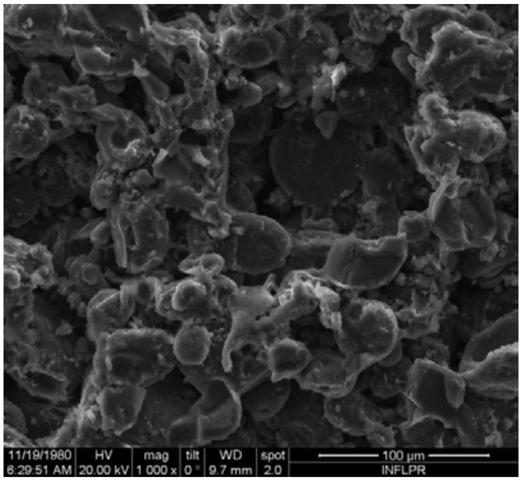
Tablets of PAN and salt were placed in a small crucible of quartz (one in the center and the other next to the edge) and placed in a programmable oven with controlled atmosphere. The samples been heat-treated slowly for 2 hours until the temperature of 400^0C in normal atmosphere. After achieving the value of temperature 400^0C, the argon(inert gas) is introduced with a supply flow of 10-15 ml / minute.

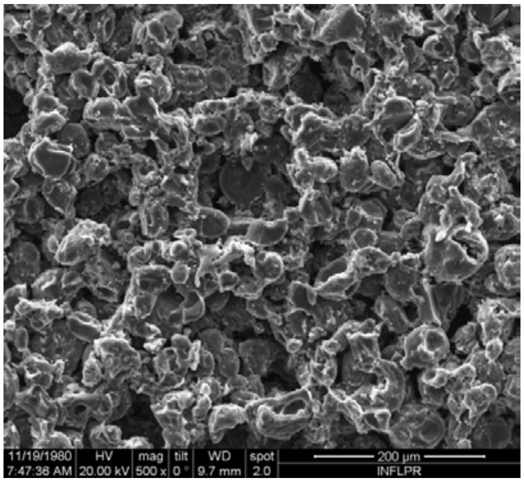
The oven value of a 400^0C was maintained constant for 30 minutes. Thereafter the oven temperature is increased up to 700^0C for one hour. Then, we keep this value of 700^0C constant for 30 minutes. Then follows a free cooling of the oven and when it achieves the value of 400^0C the argon feeding is interrupted. The samples been taken out of the oven only after free cooling to room temperature. The samples are ultra sounded in water for 3min for the dissolution of sodium chloride. The ultrasonic device is used for this operation.

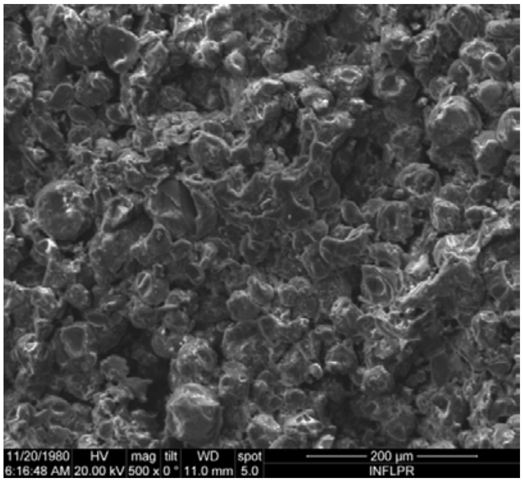
Results and Discussion

To study the morphology of the obtained carbonic materials was used SEM method - scanning electron microscopy (fig. 3-7) and Raman spectroscopy (JASCO LRS-3100) (fig. 8).









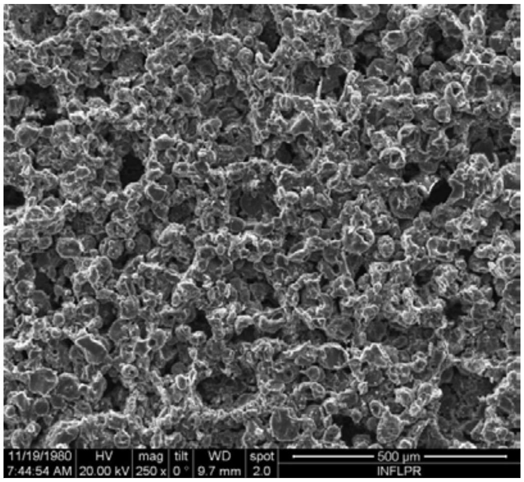


Fig. 3-7. SEM images of various samples of PAN and NaCl with details from the size of 50µm up to 500µm

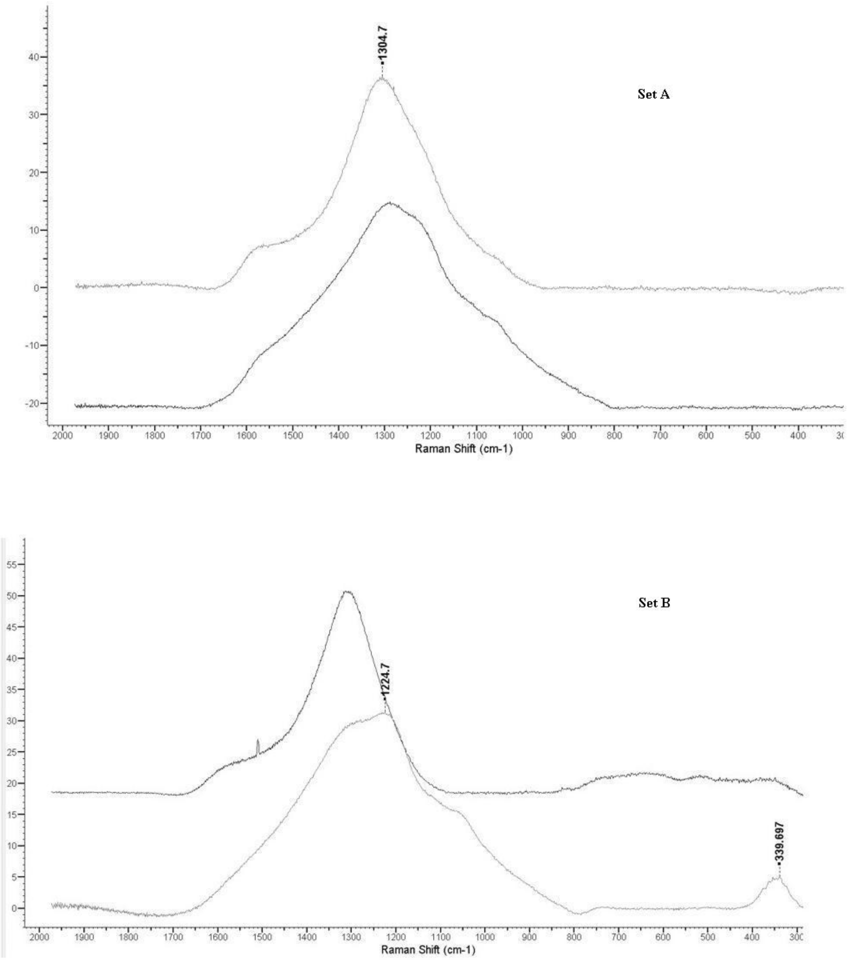


Fig. 8. Raman spectra of samples of PAN and NaCl

Following the PAN pyrolysis process results its cyclization and transformation into the pyridine rings. During the process of pyrolysis most non carbonic elements are volatilizated in the form of ammonia, cyanhydric acid, hydrogen, water, CO, CO_2 and other gases [9]. After the elimination of all volatile products, a significant loss of mass is observed (table 1 and table 2).

Table 1. The variation of pills mass (set A)

Heat treated samples	Baseline pills thickness (mm)	The value of pills mass (mg)		
		Baseline	The amount of weight after completing the heat treatment	The final value
sample 1	0,53	325,3	219,9	225,5
sample 2	0,525	325,8	237,7	226,3

Table 2. The variation of pills mass (set B)

Heat treated samples	Baseline pills thickness (mm)	The value of pills mass (mg)		
		Baseline	The amount of weight after completing the heat treatment	The final value
sample 1	0,505	319,1	183,3	180,6
sample 2	0,525	325,1	203,2	196,9

Conclusions

From SEM images can be seen that the obtained microcellular carbonic materials have a wide distribution of size of pores and an irregular structure. The Raman Spectra for the two sets of samples are different. Could be seen a peak that occurs at 1304,7 cm^{-1}ce corresponding to carbon in the amorphous state.

We see a higher degree of transformation to a peak appearing at 1600 cm^{-1} corresponding to of carbon in graphite state. For the sample 2 of the set A as well for the sample 2 of the set B is observed the same behavior grace of the temperature gradient along the oven, the PAN conversion degree is lower.

References

1. Bradshaw, W.G., Pinoli, P.C., Mitchell, M.J. - Recent Developments in glassy carbon fabrication, *Proceedings of 9th Biennial Conference on Carbon, American Carbon Society*, p. 7, Boston, USA, 1969
2. Bunnell, L.R. - Proc. Vitreous carbon matrix carbon-carbon composite by copyrolysis, *Proceedings of 12th Biennial Conference on Carbon*, Pennsylvania, American Carbon Society, pp. 333-334 Pennsilvania, USA, 1975
3. Kaplan, R.B. - Open cell tantalum structures for cancellous bone implants and cell and tissue receptors, *US Patent* 5282861, 1994
4. Rezende, M.C. - *Produção de Carbono Vítreo, em Escala de Laboratório, a partir de Resinas Furfurílica e Fenólica*, Doctoral Thesis, São Paulo, Brazil.EPUSP, 1991
5. Bokros, J.C. - Carbon biomedical devices, *Carbon*, 15(6):353, 1977
6. Jenkins, G.M., Grigson, C.J. - The fabrication of artifacts out of glassy carbon and arbon-fiber-reinforced carbon for biomedical applications, *J. Biomed. Mater. Res.*, 13, pp. 371-394, 1979
7. Schmitt Jr., J.L., Walker, P.L. - Carbon molecular sieve supports for metal catalysts-II. Selective hydrogenation of hydrocarbons over platinum supported on polyfurfuryl alcohol, *Carbon*, 10(1), pp. 87-92, 1972

8. Cooper, B.J., Trimm, D.L. - Selectivity of carbon molecular sieve supported catalysts, *Preprint 3rd Conference on Industrial Carbon and Graphite*, UK. London, *Soc. Chem. Ind*., p. 49, 1970
9. Caşcaval, C. - *Studiul polimerilor pin piroliză şi cromatografie de gaze*, Ed. Academiei Republicii Socialiste România, Bucureşti, 1983

Obținerea de carbon microcelular prin piroliza materialelor polimerice

Rezumat

Carbonul microcelular este un material avansat datorită proprietăților sale de a fi inert chimic şi de a avea conductivitate termică mare, ceea ce îl face să fie solicitat în aplicații de schimb de căldura la rate mari de transfer. În plus, carbonul rezultat din piroliza polimerilor prezintă diverse proprietăți de adsorbție la gaze, respectiv de separare a acestora. Metodele actuale de a obține carbon microcelular implică utilizarea de agenți de spumare în tratamentul termic, ceea ce conduce la formarea unei distribuții de pori neomogene. Această contribuție prezintă o nouă metodă de piroliză a polimerilor constând din tratamentul termi, al materialelor compozite polimer-săruri stabile termic. La 700^0C *structuri de carbon microcelular sunt obținute din matrici de poliacrilonitril şi sare. Structura şi proprietățile carbonului microcelular obținut în aceste condiții au fost investigate prin SEM şi Raman.*