

## Preparation of porous carbons from polymeric precursors modified with acrylated kraft lignin

**M Sobiesiak**

Department of Polymer Chemistry, Faculty of Chemistry, Maria Curie Skłodowska University, Lublin, Poland

E-mail: [magdalena.sobiesiak@umcs.pl](mailto:magdalena.sobiesiak@umcs.pl)

**Abstract.** The presented studies concern the preparation of porous carbons from a BPA.DA-St polymer containing acrylated kraft lignin as a monomer. The porous polymeric precursor in the form of microspheres was synthesized in suspension polymerization process. Next samples of the polymer were impregnated with acetic acid or aqueous solution of acetates (potassium or ammonia), dried and carbonised in nitrogen atmosphere at 450°C. After carbonization microspherical shape of the materials was remained, that is desired feature for potential application in chromatography or SPE technique. Chemical and textural properties of the porous carbon adsorbents were characterized using infrared spectroscopy (ATR-FTIR), thermogravimetry analyses with mass spectrometry of released gases (TG-MS) and nitrogen sorption experiments. The presented studies revealed the impregnation is useful method for development of porous structure of carbonaceous materials. The highest values of porous structure parameters were obtained when acetic acid and ammonium acetate were used as impregnating substances. On the surface of the materials oxygen functional groups are present that is important for specific interactions during sorption processes. The highest contents of functionalities were observed for carbon BPA.DA-St-LA-C-AcNH<sub>4</sub>.

### 1. Introduction

Porous carbon sorbents are widely used for water purification purposes for removing both organic and inorganic pollutants. The main features deciding on applicability of carbon adsorbents for sorption are porous structure and surface chemistry. Both of them are formed during thermal treatment and activation process, and strongly depend on pyrolysis conditions and the nature of precursor. [1-3]

Currently the interest in production of low-cost adsorbents is growing. This aim can be realized by utilization of low values by-products or residual materials as carbonaceous precursors.

Lignin is a substance that fulfil above requirements. Commercially, it is by-product of paper industry, but from chemical point of view possesses a great potential. Polyaromatic macromolecules of lignin with numerous functional groups can be equally precursors of carbon adsorbents as well as reagents in chemical syntheses of new polymeric materials [3, 4].

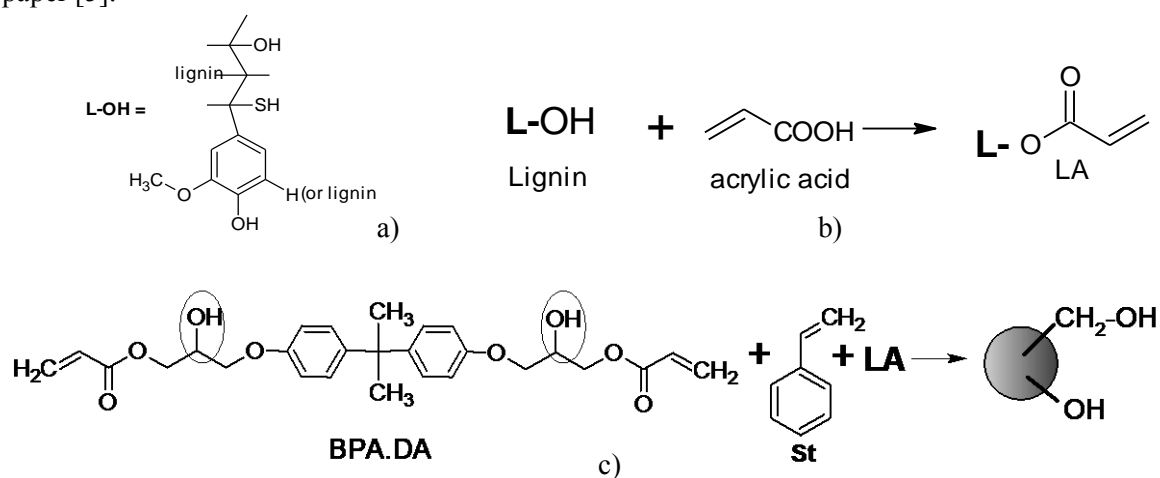
The presented studies concern the preparation of porous carbons from a polymeric composite containing acrylated kraft lignin as a monomer. The porous polymeric precursor in the form of microspheres was synthesized in suspension polymerization process. Next samples of the polymer were impregnated with aqueous solution of activating substance (acetic acid, potassium and ammonia acetates) and then carbonised at 450°C. Chemical and textural properties of the porous carbon adsorbents were characterized using nitrogen sorption experiments, infrared spectroscopy and thermogravimetric analyses coupled with mass spectrometry of evolved gases.



Porous structure and chemical properties of the prepared carbons were different in relation to substance used for activation. The results of ATR-FTIR and MS analyses revealed the presence of oxygen functional groups on the surface of the prepared carbon materials that is important for specific interactions during sorption processes. Additionally, after carbonization the materials remained their microspherical shape, what is desired feature for potential application in chromatography or SPE technique.

## 2. Experimental

The composite (BPA.DA-St-LA), used as polymeric precursor for preparation of the carbons, was synthesised from diacrylated bisphenol A (BPA.DA), styrene (St) and acrylated kraft lignin (LA), according to the scheme presented in Figure 1. In order to obtain polymer in the form of microspheres suspension polymerization process was applied. Details of this process were published in the previous paper [5].



**Figure 1.** a) Fragment of chemical structure of lignin, b) Scheme of reaction of lignin with acrylic acid, c) Scheme of synthesis of the polymeric composite - BPA.DA-St-LA, used as the precursor

### 2.1. Carbonisation process of polymeric microspheres

Samples of the polymeric precursor (BPA.DA-St-LA) were impregnated with aqueous solution of acetic acid (BPA.DA-St-LA-C-AcA) or acetates (potassium - BPA.DA-St-LA-C-AcK or ammonia - BPA.DA-St-LA-C-AcNH<sub>4</sub>). Next, they were dried in the air. Carbonization process was carried out in tubular furnace under nitrogen atmosphere (100mL/min.). The samples were heated from room temperature to 450°C with the rate 10°C/min. The final temperature was maintained for 30 min. The prepared porous carbons were washed with hot water and dried. Sample carbonized in the same conditions, but without impregnation was used as a reference material (BPA.DA-St-LA-C). After carbonization all prepared carbons maintained spherical shape except for BPA.DA-St-LA-C-AcK.

### 2.2. Apparatus

Carbonisation processes were performed in tubular furnace (Czylok, Poland) with quartz reactor tube.

The porous structure of prepared materials were characterised by nitrogen adsorption at 77K using an adsorption analyser ASAP 2405 (Micrometrics Inc., USA). Before analysis the samples were outgassed at 140°C for 2 h. Specific surface areas were calculated by the BET method, assuming that the area of a single nitrogen molecule in adsorbed state is 16.2 Å<sup>2</sup>. Pore volumes and pore size distributions were determined by the BJH method.

ATR-FTIR (Attenuated Total Reflectance) spectra were obtained using a Bruker FTIR spectrophotometer TENSOR 27. The spectra were acquired in the spectral region 400-4000 cm<sup>-1</sup>. Resolution was set as 4 cm<sup>-1</sup> and number of scans per spectrum was 32.

TG-MS (Thermogravimetry coupled with Mass Spectrometry of evolved gasses) analyses were performed on the thermal analyzer STA 449 F1 Jupiter (Netzsch, Selb, Germany). Measurements were carried out at the heating rate of 10°C/min in the temperature range 30-1000°C under helium atmosphere (40 mL/min). Gaseous products evolved of the sample at the time of heating were analyzed by on line coupled QMS 403C Aeolos (Netzsch, Germany).

### 3. Results and Discussion

Characteristics of the carbonised materials were performed in comparison to the reference carbon material (BPA.DA-St-LA-C) and the polymeric precursor (BPA.DA-St-LA).

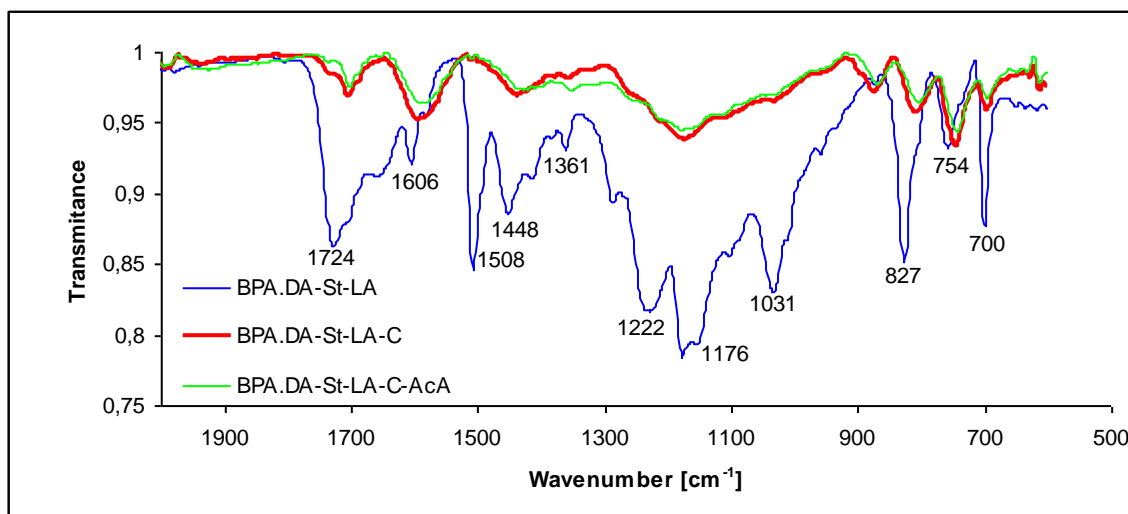
Table 1 summarise porous structure parameters of the studied materials. The highest values of specific surface areas ( $S_{\text{BET}}$ ) and total pore volumes ( $V_{\text{TOT}}$ ) were obtained for the carbons impregnated with acetic acid and ammonia acetate. Development of porosity ( $S_{\text{BET}}$ ) in these two cases was ca. 50 and 80 times larger in comparison to that of the polymeric precursor. Similar tendency was observed for values of total pore volumes. Although, porous structure of the presented materials is quite different. The polymeric precursor in its structure possesses pores of width in the range of 3 to 15nm. Carbonization without any impregnation agent resulted in shrinking of pores, and consequently porous structure of BPA.DA-St-LA-C was dominated by small mesopores (2.8nm). In the case of carbons activated with acetic acid and ammonia acetate, pore size distribution possesses bimodal character. However, pores of BPA.DA-St-LA-C-AcA had a little larger widths then those of BPA.DA-St-LA-C-AcNH<sub>4</sub>. Mean pore size of BPA.DA-St-LA-C-AcK was ca. 33nm.

**Table 1.** Porous structure parameters of the studied materials

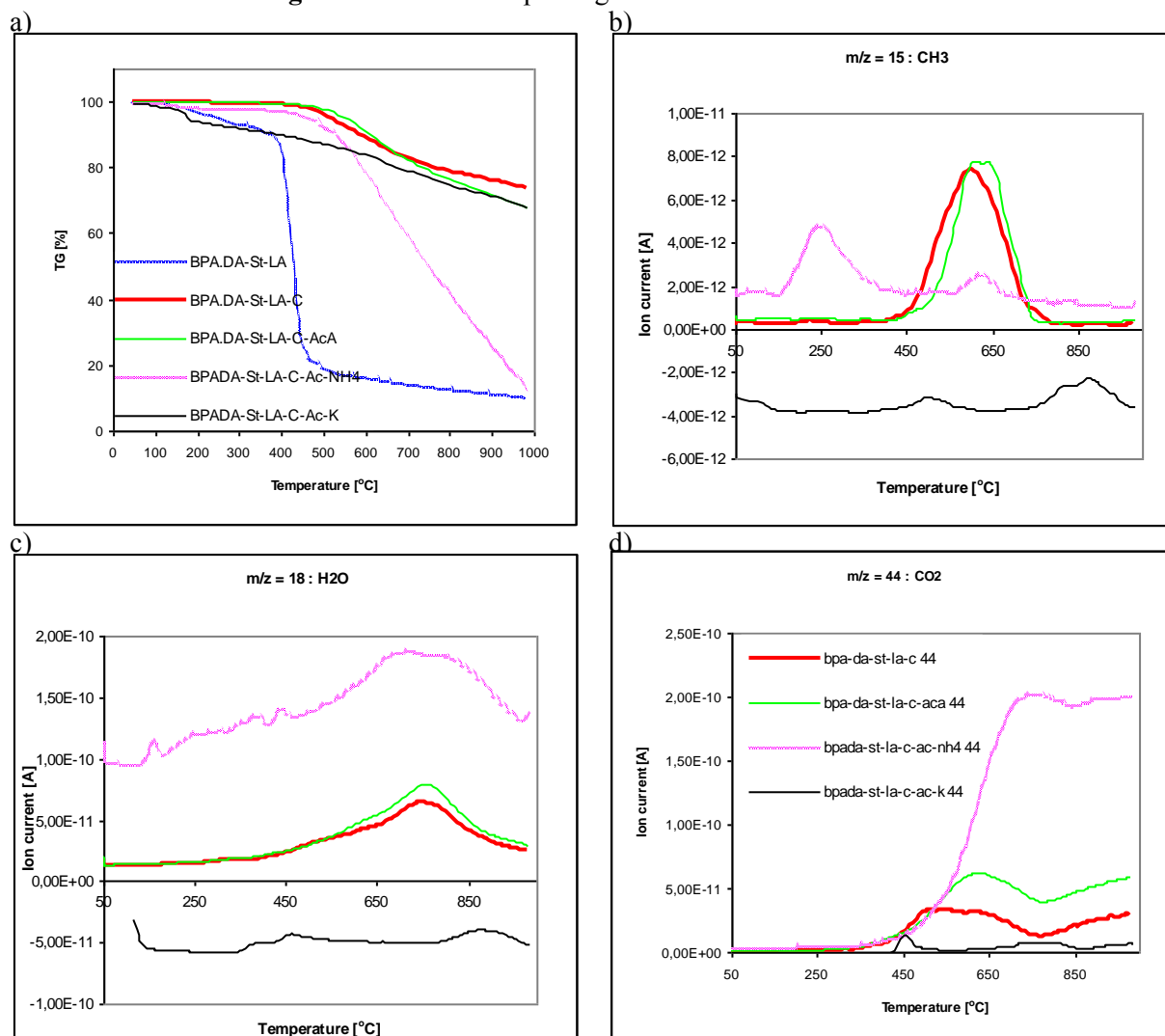
material	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{\text{TOT}}$ (cm <sup>3</sup> g <sup>-1</sup> )	Pore size (nm)
BPA.DA-St-LA	3	0.025	3-15
BPA.DA-St-LA-C	5	0.018	2.8
BPA.DA-St-LA-C-AcA	155	0.090	13.5; 37.7
BPA.DA-St-LA-C-AcNH <sub>4</sub>	244	0.117	4.5; 28.7
BPA.DA-St-LA-C-AcK	9	0.074	33

Chemical structures of the prepared materials were evaluated on the basis of ATR-FTIR analyses (Fig. 2) and results of mass spectrometry analyses of evolved gases (Fig. 3 b)-d)).

In the ATR –FTIR spectra of polymeric precursor numerous bands coming from functional groups are present. Signals of ester groups: 1724, 1285, 1100 cm<sup>-1</sup>; carboxylic: 1650, 1360 cm<sup>-1</sup>; ether: 1222, 1031 cm<sup>-1</sup>; hydroxyl: 1200-1050 cm<sup>-1</sup>; aromatic rings: 1606, 1508, 827, 754, 700 cm<sup>-1</sup>; methyl and methylene groups: 1448, 754 cm<sup>-1</sup> are observed. After carbonization quantity of these species decreased, but carboxylic, ester and hydroxyl groups were still present in polyaromatic structure of the prepared carbons.



**Figure 2.** ATR-FTIR spectrograms of chosen materials



**Figure 3.** a) Thermogravimetric curves of the studied materials, mass spectrometry curves of the evolved gases for b)  $m/z = 15$ , c)  $m/z = 18$ , d)  $m/z = 44$ , respectively

These data were also confirmed by TG-MS analyses. Different functionalities decompose in specific range of temperatures evolving molecules of simple substances such as CO<sub>2</sub>, CO, H<sub>2</sub>O, hydrocarbons, etc observed as peaks on MS-profiles [6]. Typical decomposition temperature of carbonyl groups is in range of 700 to 900°C, ethers at ca. 700°C, carboxylic anhydrides about 400 and 600°C, carboxylic acids 100-400°C, and hydroxyl groups 600-700°C. The strongest signals of CO<sub>2</sub> are in the range of 350-700°C, and for H<sub>2</sub>O in range of 300-900°C. These data prove the presence of hydroxyl, ester, carboxyl and carbonyl groups. Signals of simple hydrocarbons are observed at decomposition temperature of materials, that for the carbons activated with acid and the reference one is 450-700°C, for the carbons activated with ammonia acetate is 250 and 600°C, whereas for activated with potassium acetate - 500 and 800°C.

The highest contents of functional groups possessed BPA.DA-St-LA-C-AcNH<sub>4</sub>.

#### 4. Conclusions

The presented studies revealed the impregnation is useful method for development of porous structure of carbonaceous materials. The specific surface areas were ca. 30 and 50 times larger than that of the reference carbon, if acetic acid and ammonium acetate were used as activators.

All prepared carbons were mesoporous. Mean pore diameters of the carbons impregnated with acetic acid were 13.5 and 37.7 nm, and with ammonium acetate – 4.5 and 28.7 nm.

TG-MS profiles and FTIR-ATR spectra proved the presence of: ester, acid anhydride, carboxylic, hydroxyl (both aromatic and aliphatic) functional groups. The highest contents of functionalities were observed for carbon BPA.DA-St-LA-C-AcNH<sub>4</sub>.

#### 5. Acknowledgments

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement No PIRSES-GA-2013-612484

#### References

- [1] Sobiesiak M 2012 *Adsorption* **19** 349
- [2] Puziy A M, Poddubnaya O I, Sobiesiak M, and Gawdzik B 2013 *Adsorption* **19** 717
- [3] Myglovets M, Poddubnaya O I, Sevastyanova O, Lindström M E, Gawdzik B, Sobiesiak M, Tryba M M and Puziy A M 2014 *Proceedings of 5th NWBC, March 25th-27th, 2014*. Stockholm, Sweden
- [4] Stewart D 2008 *Industrial Crops and Products* **27** 202
- [5] Gawdzik B, Sobiesiak M, Podkościelna B and Sevastyanova O 2014 *COST Action FP1105 "Understanding Wood Cell Wall Structure, Biopolymer Interaction and Composition: Implications for Current Products and New Material Innovation,"* 52
- [6] Stein A, Wang Z and Fierke M A 2009 *Advanced Materials* **21** 265