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Functional starch based carbon aerogels for energy applications

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Abstract

Nanoporous carbon aerogels were synthesized by the carbonization of organic aerogels, derived from a sol-gel polymerization using various types of starch and followed by an ambient pressure drying. Optimal conditions for pyrolysis of organic aerogels were determined by TG/DTG/SDTA analysis. The structure and the morphology of the prepared carbon aerogels were investigated using XRD and N_2-BET measurements respectively. Electrical properties of the obtained aerogels were examined by EC studies. Prepared carbon materials revealed high surface area and good electrical conductivity. Thus, one can say that carbon aerogels exhibit potential as new materials for energy applications (eg. supercapacitors, Li-ion batteries, etc.).

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Keywords: carbon aerogels; starch; sol-gel polycondensation; textural properties; electrical conductivity

1. Introduction

Carbon aerogels are a novel class of nanostructured carbon materials with a continuous solid framework and an open pore structure that have been extensively studied during the last decade [1,2]. These materials exhibit unusual properties including low density, well-defined and controlled pore structure, large surface area, mechanical strength and high electrical conductivity which make them innovative and promising materials for energy applications [3-5].

These highly porous carbon materials can be obtained in different forms by the pyrolysis of organic aerogels at elevated temperatures under an inert atmosphere. The most commonly used organics for the preparation of the carbon aerogels via a sol-gel polycondensation are resorcinol and formaldehyde [6]. However, the use of natural

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polysaccharides and their derivatives is considered to be more attractive due to their availability, renewability, stability, non toxicity and low cost [7-10].

One of the most abundant polymers that occur in nature is starch. It is found mainly in the leaves, seeds and tubers of many vegetables (eg. potato, pea, wheat, tapioca, etc.). At a molecular level, the native starch is made of two distinct components, amylose and amylopectin. Both elements contain polymer chains of glucose units, but the chains are linked in a different way. Amylose is mainly linear, whereas amylopectin has a highly branched, very dense structure [11]. The relative proportion of these two constituents varies as a function of the starch source and influences the gel formation.

In the present study, carbon aerogels based on natural starches of different botanical origin (potato, maize and rice) were characterized in terms of structural, textural and electrical properties. To avoid the pore collapse, decrease the processing cost and shorten the preparation time, an ambient pressure drying instead of supercritical CO_2 extraction was applied.

2. Experimental

Starch based carbon aerogels were prepared by the carbonization of organic aerogels. Four main steps can be distinguished in the fabrication of these materials, and the first was the polycondensation process in which different types of starches (potato, maize and rice) with appropriate dilution ratio were dispersed in water and stirred while maintaining the suitable gelatinization temperature for each type of starch. The second step was the solvent exchange carried out either by immersing the aqueous gels for few days directly in the new solvent – ethanol, in order to replace water trapped inside the pores, thus alcogels were formed. The third step was the alcogels drying performed at 50 °C for 1 day under ambient pressure and the fourth step was the pyrolysis of organic aerogels conducted for 6 h with a constant flow of argon at 600 °C and after that carbon aerogels were obtained.

The gelatinization temperature of starch is one of the most important parameters for gelatinization process and during this study was determined by differential scanning calorimetry (DSC). The DSC experiments were performed in a Mettler Toledo 821^e microcalorimeter equipped with intracooler Haake in aluminum crucibles within temperature range of 40 ÷ 100 °C with a heating rate equal to 10 °Cmin^{-1}.

Thermal analysis methods (TG/DTG/SDTA) were used to establish the optimal conditions for the carbonization process of organic aerogels. The TG/DTG/SDTA measurements were performed in a Mettler Toledo 851^e microthermogravimeter in aluminum crucibles with an argon flow (80 mLmin^{-1}) from 25 to 1000 °C with a heating rate of 10 °Cmin^{-1}.

The crystal structure of the resulting carbon materials was analyzed by X-ray powder diffraction (XRD) in a Bragg - Bretano geometry on BRUKER D2 PHASER using Cu K_α radiation (λ = 0.154184 nm) in the range of 10 ÷ 60 ° (2θ).

Textural properties of the starch-based carbon aerogels were investigated by low-temperature nitrogen adsorption–desorption measurements using Micromeritics ASAP 2020 analyzer. Prior to the measurements, prepared samples were evacuated at appropriate conditions. Specific surface area was determined by the BET (Brunauer - Emmett - Teller) method while pore volume and average pore diameter were estimated using the BJH (Barrett - Joyner - Halenda) method.

The electrical properties of the obtained aerogels were examined by the electrical conductivity studies (EC) using 4-probe AC method within temperature range of -20 to 40 °C.

3. Results and Discussion

Fig. 1 presents the DSC results generated for different types of starch with 50% (by weight) of distilled water. The occurrence of the endothermic curves indicates that a first order transition of polysaccharides takes place during gelatinization upon heating. It is apparent that different profile patterns appear for each starch (potato PS, maize MS and rice RS).

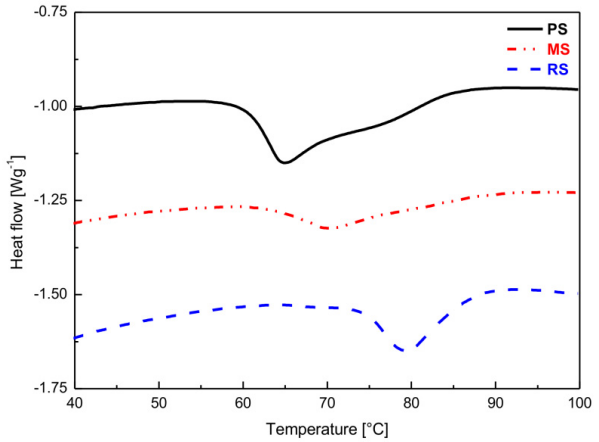

Fig. 1. DSC results on the gelatinization of different types of starch.

Data on the thermal transition enthalpies of starches and the gelatinization temperatures are presented in Table 1.

Table 1. Summary of the gelatinization parameters for the various starches.

Sample	T_{onset} (°C)	T_{peak} (°C)	ΔH (Jg^{-1})
PS	60	65	7.7
MS	63	71	2.7
RS	74	79	2.5

Exemplary TG/DTG/SDTA curves of organic aerogel prepared from potato starch are shown in Fig. 2. The first slight mass loss (5%) is related to the physical process of water desorption from the aerogel structure and occurs below 150 °C. The second stage of mass loss (75%) is attributed to the consequent carbonization reaction in the organic aerogel and is accompanied by a strong endothermic effect. The pyrolysis starts in a relatively low temperature and leads to the formation of the carbonaceous materials.

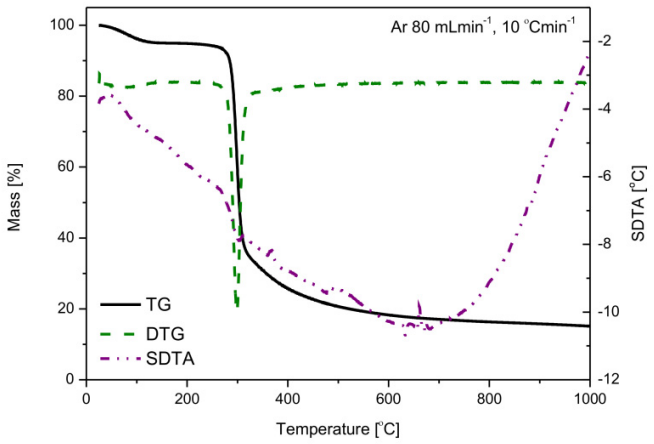

Fig. 2. The TG/DTG/SDTA analysis of potato starch aerogel.

The X-ray diffraction patterns of different carbon aerogels (CAG) obtained from potato, maize and rice starch precursors are illustrated in Fig.3.

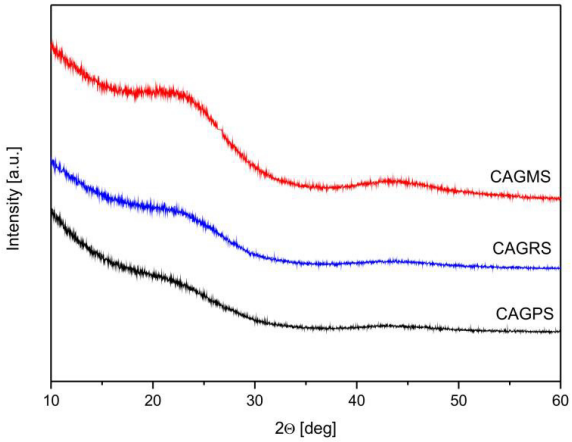

Fig. 3. XRD patterns of carbon aerogels.

The two broad humps, centered at 2θ = 23 and 43 ° for all the CAG samples were found to be almost identical. These reflections correspond to the graphitic phase of carbon [12] and indicate that prepared carbon materials are partially crystalline materials and have pseudo graphitic structure.

A representative N_2 adsorption-desorption isotherms of the carbon aerogels are depicted in Fig. 4. Sharp rise at the initial part of the isotherms indicates the presence of micropores in the carbon materials.

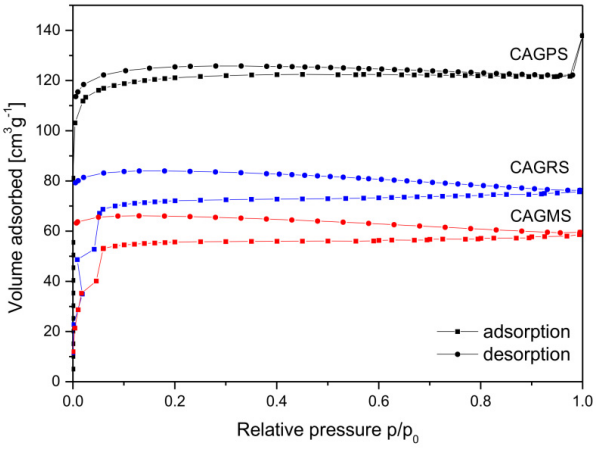

Fig. 4. N_2 adsorption-desorption isotherms of carbon aerogels.

According to the isotherms, the surface area, pore volume and average pore diameter of the samples were calculated and collected in Table 2. It is noticeable that carbon aerogel prepared from potato starch presents the highest BET surface area as well as pore volume and average diameter of pores corresponding to the lowest crystallinity of the CAGPS sample, as was shown in the X-ray diffraction study.

Table 2. Description and texture characteristics of carbon samples.

Sample	Description of the sample	S_{BET} (m^2g^{-1})	V_p (cm^3g^{-1})	D_p (nm)
CAGPS	carbon aerogel based on potato starch	370.5	0.037	6.9
CAGMS	carbon aerogel based on maize starch	169.4	0.009	3.5
CAGRS	carbon aerogel based on rice starch	220.7	0.019	2.6

The temperature dependence of conductivity for CAG samples is shown in Fig. 5 in the log σ vs. $1000T^{-1}$ coordinates. In Table 3, values of electrical conductivity at around 25 °C and the activation energy in the -20 to 40 °C temperature range are listed. It is seen that carbon aerogel made from potato starch has the lowest value of electrical conductivity while the carbon material derived from maize starch exhibits the highest σ value of all prepared samples what is also related to the highest crystallinity and lowest BET surface area.

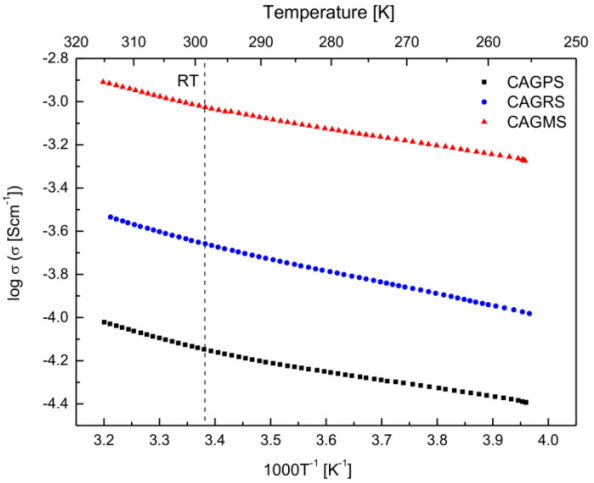

Fig. 5. Electrical conductivity of CAGPS, CAGRS and CAGMS samples.

Table 3. Electrical properties of the synthesized carbon aerogels.

Sample	σ at ~25 °C (10^{-4} Scm^{-1})	E_a (eV)
CAGPS	0.75	0.09
CAGMS	9.90	0.09
CAGRS	2.31	0.11

4. Conclusions

Carbon aerogels were successfully synthesized through the gelatinization process of natural starches (potato, maize and rice) followed by the carbonization of organic aerogels. This method made it possible to obtain nanostructured tailored carbon materials with well-developed porosity and high surface area. The electrical conductivity measurements proved that prepared materials provide good electrical properties. It was also investigated that the textural and electrical properties of the final carbon materials depend on the botanical origin of starches and can be easily modified as a function of different synthesis and pyrolysis parameters.

Concluding, the outcomes of the XRD, N_2-BET and EC measurements of starch based carbon aerogels are closely associated and point out that higher crystallinity and lower BET surface area of the samples lead to the high value of electrical conductivity along with the low activation energy. The obtained carbon aerogels seem to be prospective materials which can be used for energy applications.

Acknowledgements

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