MONITORING OF RELEASED PARTICLES BY HEATING RF POLYMER FOR CONVERSION TO CARBON UNDER INERT ATMOSPHERE

Kristýna HRABOVÁ, Ján POLÁČIK, Vladimír ADAMEC, Barbora SCHÜLLEROVÁ, Ladislav ŠNAJDÁREK, Jiří POSPÍŠIL

Brno University of Technology, Brno, Czech Republic, EU

Abstract

Monitoring and counting of the fine particles released during the temperature rise of the resorcinol-formaldehyde polymer suitable for conversion to carbon aerogel are discussed in the poster. Carbon aerogel is produced by heat treatment under inert atmosphere. The presented approach combines the thermogravimetric analysis with detailed monitoring of the size distribution of fine particles produced. Thermogravimetric analysis (TGA) allows the exact temperature influence of the sample and identifies its weight loss. Aerosol stream leaving TGA enters a Scanning Mobility Particle Sizer (SMPS) where the particle size fractions are separated. A number of particles in the particles size fractions are identified by the condensation particle counter (CPC). Long-term use of Carbon Aerogels results in degradation of these materials and release of fine particles, which could be harmful to health.

Keywords: Carbon, aerogel, thermogravimetrics, aerosol monitoring, fine particles

1. INTRODUCTION

Aerogel is a solid substance with the lowest known density. One cubic meter of the latest and lightest variation of this material weighs mere 1.9 grams. It is also called „solid smoke“ as up to 99.8 % of its volume is air. Aerogel is the only material with porosity over 95 % and a very wide pore distribution. The pores are open, i.e. gases or liquids can penetrate the material with minimal limitations. Aerogels have a low coefficient of thermal conductivity ranging from λ= 0.015 to 0.020 W/m.K [1,2]. Aerogels are used for catalytic reactions, production of microfiltration membranes, adsorbents etc. Thanks to high surface area, they can absorb toxic and oil substances found in water. Substances with high surface area, thermal stability and the ability to adsorb heavy metal ions from aqueous solutions are used as adsorbent materials. Aerogel is made by thermal removal of liquid from the substance. They are prepared through sol-gel polycondensation of suitable organic monomers such as resorcinol and formaldehyde producing organic gel. The solid structure formed in this way is filled with liquid phase which is replaced with air through drying. During this process, organic aerogel is created, and it subsequently becomes carbonaceous aerogel through pyrolysis, which allows a wide application spectrum as adsorbents, catalyst carriers or super-condensers. During its production, like during other processes subject to heat treatment, ultrafine particles are released including PM_1 particles. Types of aerogels Oxides (Quarz, Titania, Zirkonia, Mixed oxides), Polymers (Resorcinol, Melamine-Formaldehyde), Carbon (pyrolysed Polymer), cellulose, starch, alginates, and almost everything that can be gelled [3,4,5].

2. SAMPLES AND MATERIALS

To produce carbon-aerogel in our experiment we heated a sample of resorcinol-formaldehyde polymer in nitrogen internal atmosphere to 850 °C. During this process we monitored the weight loss of the sample using thermogravimetric analysis. At the same time, we detected emerging fine particles using SMPS (Scanning Mobility Particle Sizer). For comparison, we used a similar approach for a sample of pure carbon.

Carbon aerogels are a unique group of artificially prepared carbonaceous materials, whose main component is air (95 vol.%) dispersed in their solid structure. Carbon aerogels are highly porous amorphous carbon

materials that are derived from organic aerogels. They consist of interconnected clusters of carbon nanoparticles with diameters ranging from 1 to 20 nm. To transform organic aerogels to their carbon form, a pyrolysis or carbonization process in an inert gas atmosphere (nitrogen, argon, or helium) at temperatures above 600 °C is necessary. Carbon can be included in many inorganic nanostructures to produce nanocomposites with considerably better electronic, chemical, thermal, and mechanical properties. Our sample was compressed from expanded graphite with carbon purity of 99.85 %. The sample was compressed into tablets [6,7].

3. EXPERIMENTAL SETUP

3.1. Thermogravimetric analysis (TGA)

The laboratory procedure which was developed combines thermogravimetric analysis with detailed monitoring of the size distribution of the fine particles produced. Thermogravimetric analysis (TGA) allows monitoring the exact temperature influence of a small fuel sample according to the desired schedule. TGA also influences the composition of the atmosphere flowing around the sample. During the measurement, the entire module is inserted into a gas-tight laboratory furnace with controlled heating rate. In our case, the atmosphere was composed of pure nitrogen. During the experiment, TGA monitors the weight of the heated sample and identifies its weight loss. The result of the measurement is a TGA curve showing the weight change in dependence on the temperature of the sample. From a subsequent analysis of the graph drawings, it is possible to obtain information on the processes taking place in the sample such as endothermic and exothermic reactions, thermal decomposition of a particular substance etc. Gaseous substances released from the sample monitored in a TGA instrument are cooled to the ambient temperature and they leave through a hose attached to an SMPS device, where the number and size of fine particles are monitored.

3.2. Scanning Mobility Particle Sizer (SMPS)

Based on the electrical mobility diameter (D_{EM}), we use the SMPS method (Scanning Mobility Particle Sizer) to measure the size of particles and their concentration. Such an apparatus consists of an impactor for separation of particles larger than $PM_{10,}$ and a neutralizer for electric charge redistribution, a DMA and a CPC. DMA - Differential Mobility Analyzer is used for particle classification based on electric mobility. It consists of two cylinder-shaped electrodes. The particles fly into the interspace of the electrodes and based on the height of the voltage and the particle charge, the SMA device releases monodisperse aerosol. CPC - Condensation Particle Counter is a device for detecting the number of monodisperse particles. The particles are too small to be detected using the optical method. That is why the particles first go through saturated butanol vapours. Then they are cooled, and they grow to the size of over 1 μm, which allows their optical laser detection (**Figure 1**).

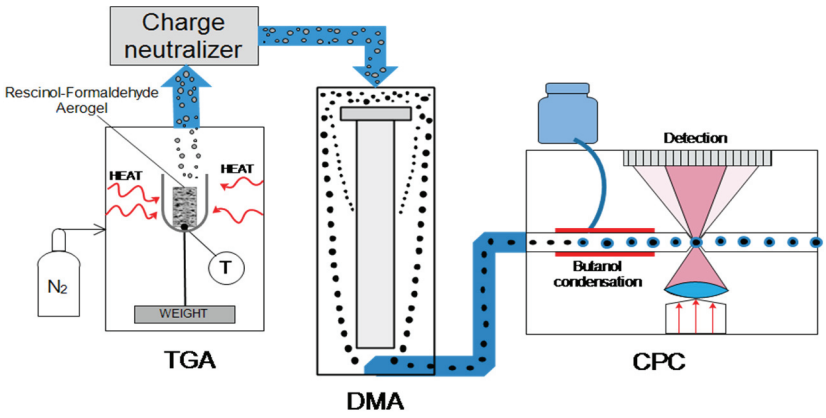

Figure 1 Experimental setup - on the left: Thermogravimetric analysis; on the right - an SMPS device

The SMPS device provides the number of fine particles and their size distribution in one-minute intervals. In this experiment, we detect particles whose size ranges from 18nm to 533nm. The minute particle distributions are shown in the colour diagram with temperature curves, sample weight and derivation (DTG) for a clearer display.

4. RESULTS

Samples of resorcinol-formaldehyde polymer and pure carbon differed in weight, but they were heated under the same conditions of inert nitrogen atmosphere at the speed of 15 Kelvin per minute to the temperature of 850 °C as shown in the **Table 1**.

Table 1 Properties of the samples examined and their weight change

	Aerogel	**Carbon**
Original sample weight	93.47 mg	584.74 mg
Weight after heating	40.04 mg	565.86 mg
Residual mass	42.84 %	96.77 %
Temperature of the largest weight loss	273 °C	200 °C
Temperature increase	15 °C / min	
Maximum temperature / endurance	850 °C / 4 hours	

As **Figure 2** shows, the change in the carbon sample is minimal, only to 96.8 % of its original weight. This proves that in higher temperatures in inert atmosphere pure carbon compressed from expanded graphite is stable. The DTG curves do not show a significant weight loss, which confirms that under these conditions there are no significant exothermic or endothermic reactions taking place in the graphite sample. We suppose that the slight weight loss is mainly caused by the release of moisture bound in the carbon sample.

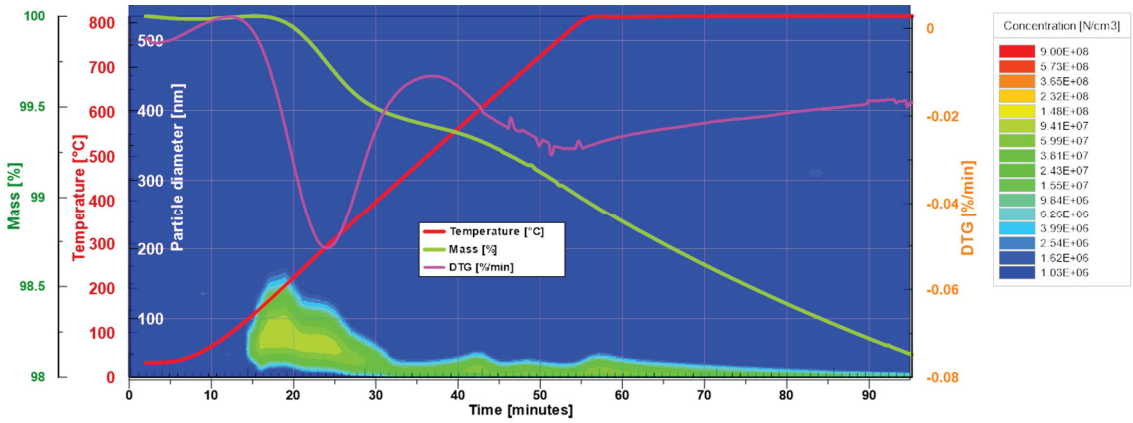

Figure 2 Diagram of fine particle production in time with temperature, weight loss and DTG for carbon curves

The production of fine particles was also minimal compared with the resorcinol-formaldehyde polymer and it already started at 110 °C. Mainly small size particles of up to 200 nanometres are produced in the nucleation and condensation modes. The maximum particle concentration was approximately 1.00E+08 particles per cm^3.

For the resorcinol-formaldehyde polymer, the weight fell as low as 40 % of the original weight after the sample was heated. A significant weight reduction occurred at around 100 °C. However, the most considerable weight loss occurred between 300 °C and 600 °C.

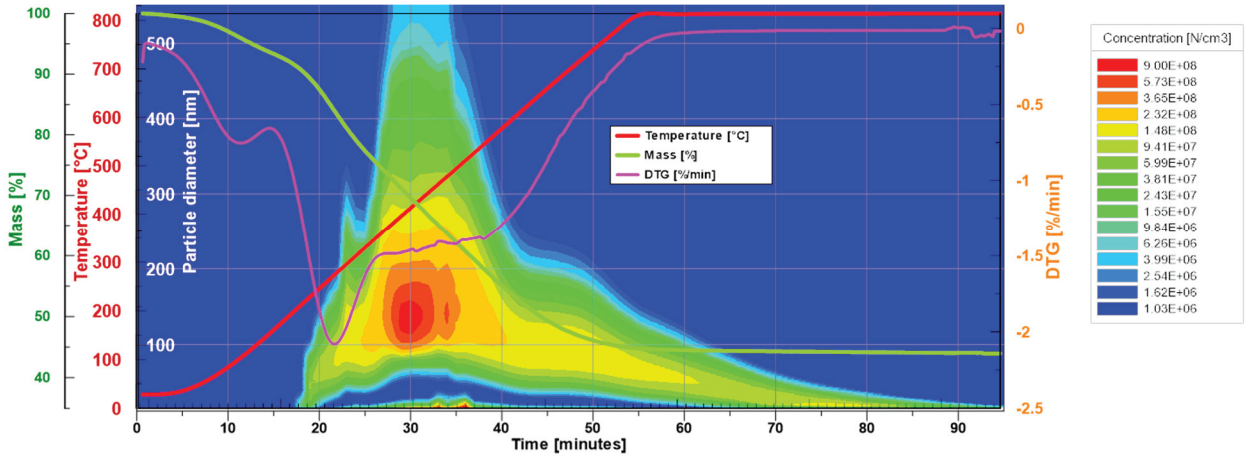

Figure 3 Diagram of fine particle production in time with temperature, weight loss and DTG for resorcinol-formaldehyde polymer curves

The production of fine particles monitored using the SMPS method was the most significant at temperatures ranging from 200 to 800 °C. The highest concentration of fine particles was detected at around 400 °C, specifically up to 9.00E+08 particles per cm^3.

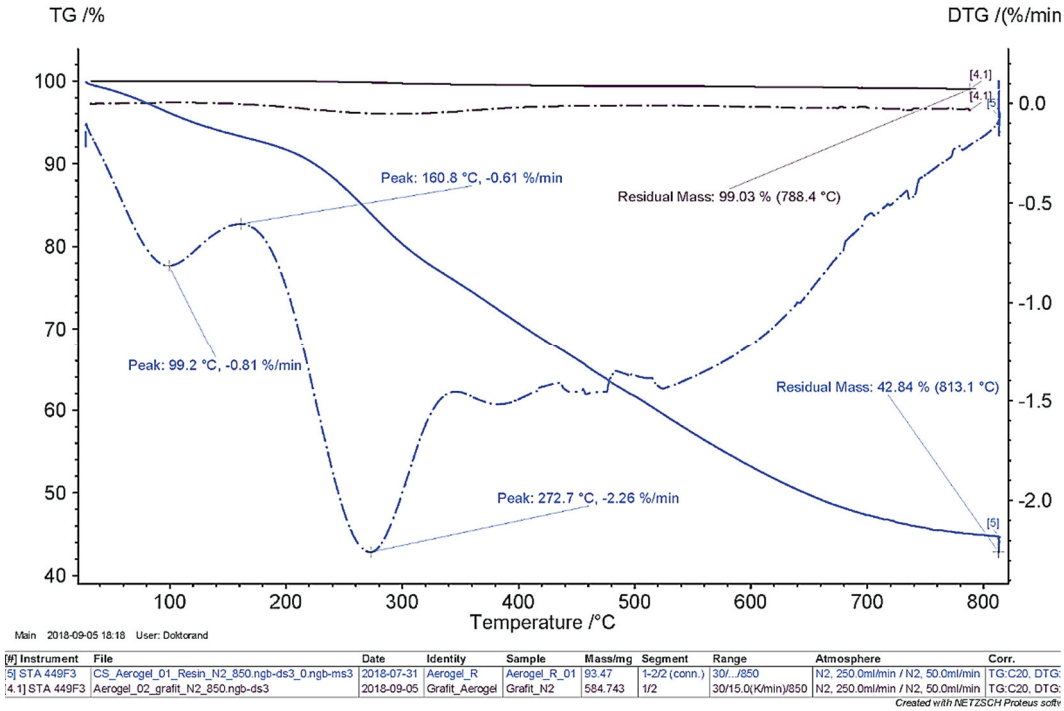

Figure 4 Comparison of the TGA and DTG curves for resorcinol-formaldehyde polymer (blue) and carbon (purple)

CONCLUSION

In this experiment, we monitored the behaviour of a heat-affected sample of resorcinol-formaldehyde polymer, which is the input product in the production of aerogel, in comparison with pure carbon. The new SMPS particle detection method was used, and weight loss was monitored using TGA analysis. We discovered that the production of ultrafine particles is higher for RF than for pure carbon and the particles also differ in size. The RF sample shows residual weight of 43 % after heat treatment, which is a considerable difference in

comparison with pure carbon (96 %). Fine particles produced during combustion and heat treatment of various products are a current issue. Their presence in the atmosphere may have a serious impact on human health, especially the respiratory system.

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