

On the development of an optimized process for the printing of high specific surface carbon adsorbing microspheres in multilayer assemblies of improved gas-barrier properties for environmental and packaging applications

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Abstract

High specific surface area, spherical activated carbons constitute a family of materials that have been widely used over the last few decades in numerous applications where the purification of a medium (i.e. water or air stream) is of outmost importance. High surface area (2400 m²/g) spherical activated carbon adsorbents (SACA) were prepared, derived from cross linked polystyrene, in mixtures with KOH up to 900 °C, in an inert N₂ atmosphere. Impregnation of SACA samples with metal salts of Sn, Ni, Fe, and Co was carried-out aiming to the development of materials with catalytic degradation and chemisorption capability. Furthermore metal salts of Cu and Zn were applied with the prospect to upgrade the SACA by introducing bactericidal / bacteriostatic properties and the subsequent development of a biomaterial system. The microspheres were printed on a number of substrates including carbon-fiber based fabrics from thin and superthin fibers of various textures. The overall objective was the development of multilayer (film and fabric assemblies) biomaterial system of improved gas-barrier and bactericidal properties for use in environmental, medical and packaging applications. The current study briefly outlines the preparation and characterization of the respective multilayer material system and presents the printing process developed for the formation of the SACA monolayer and its integration in the bio-material multilayer assembly. Finally, a number of parameters necessary for the optimization of the process are discussed.

Keywords

High specific surface carbons, multilayer assemblies, material development, printing process development, characterization, optimization.

1. Introduction

Activated carbon (AC) is a term that refers to carbon-based materials that exhibit a well integrated porous network and a high specific surface area [1]. According to Bansal [2], these attributes ensure that ACs exhibit excellent adsorption properties and make the AC material family extremely useful for many applications such as distillation, liquid and gas purification processes, decolorization, as well as biomedical, packaging and other applications in various technological areas.

Spherical Activated Carbon Adsorbents (SACAs) are primarily consisted from carbon (in the order of 90–97%) [2]. However, many other elements are also present in their structure,

either as trace elements or primary structural components such as H, O, N, and S. Functional groups (such as -OH, -C=O, -C-O-C-) are also present. These are usually introduced with the prospect of replacing the carbon atoms and as a means of tailoring or optimizing the SACA (or AC) material properties with respect to specific application. Functional groups are either present in the raw material (and subsequently enriched during the synthesis process), or are developed and/or side-produced during the synthesis and thermal elaboration of the SACA material [3,4].

In general, there exist two general types of SACAs: a) grainy activated carbon materials (GAC) with particles bigger than 0.8 mm and b) powder activated carbon (PAC) with smaller carbon particles. Usually GAC has smaller pores and a higher specific surface than PAC.

2. Synthesis and modification of SACA

Four series of spherical activated carbon samples, which have been impregnated with various metals (Fe³⁺, Co²⁺, Ni²⁺, Sn⁴⁺), were prepared using cross-linked polystyrene (commercial polymeric catalyst Purolite CT-275) as the precursor. The purpose of this process was the study and optimization of the effect of the carbonization temperature and the metal salt impregnation on the physicochemical properties of the SACA samples [5]. For this reason three different carbonization processes were used changing temperature (400 °C, 600 °C and 800 °C) and a fourth in which chemical activation with KOH was carried-out. The primary objective was the preparation of SACA material with optimal adsorption properties and bactericidal and bacteriostatic attributes. This was accomplished as there was a significant increase in the specific surface area of the precursor material from 1282 m²/gr to 2400 m²/gr in the thermally elaborated SACA spherules and prior to impregnation by metal salts. The N₂ isotherms of the SACA samples developed were measured by means of an Autosorb-1 Quantachrome nitrogen porosimeter with krypton upgrade. The overall sensitivity of the instrument did not allow for a more precise measurement of the specific surface area of the SACA material as the 2400 m²/gr represented its outmost measurement capability. The overall process and detailed results obtained are presented elsewhere and are out-of-the-scope of the current study [6,7].

3. Development of multilayer-assembly & process optimization parameters

The primary objective of the current study was the development of a an adsorptive multilayer film/fabric/filter

assembly in which a monolayer of packed, 2-D constrained, printed SACA spherules provided the active adsorbing and filtering component of the assembly. The assembly is graphically depicted in Fig. 1. Similar multilayer material systems are used in biomedical, environmental and packaging applications and the overall approach is also followed for the development of suits and garments for nuclear, biological, chemical and other hazardous environments.

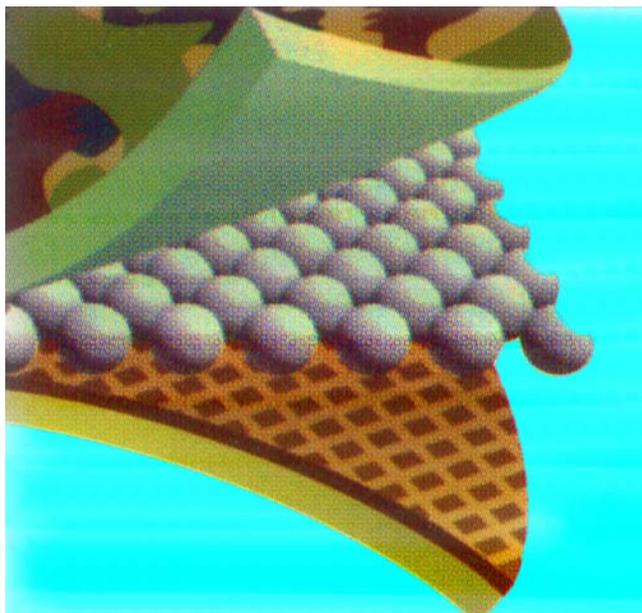


Figure 1: A schematic representation of the multilayer assembly with the printed SACA active monolayer.

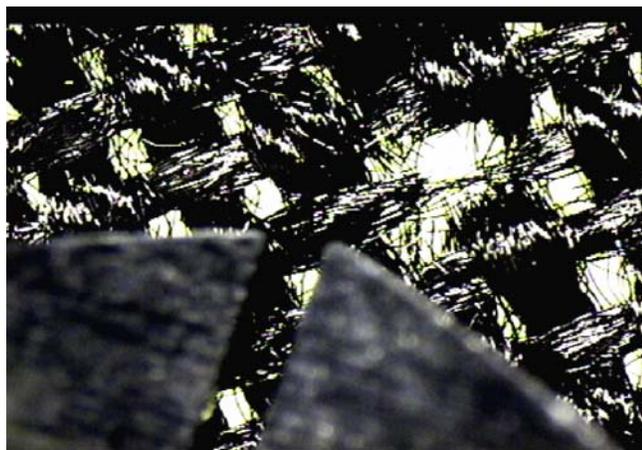


Figure 2. 100% Polyester textile was the printing substrate of the SACA monolayer

Polymer textiles (100% polyester) of different textures were used as the printing substrate for the SACA spherules (Fig. 2).

In this manner, two different plain weaves (one dense and one sparse) of the same textile were used as a means to determine the effect of the textile material to the overall adsorptive attributed of the active monolayer. The pilot unit and the various stages of the process that was developed for the production of the samples may be depicted graphically in Fig. 3. Overall, the pilot unit allows for

2 or 4 different textiles (points 1, 13 in Fig.3) to be used for the development of the multilayer assembly filter assembly, two of which functioning as the substrate and constraining layers of the active SACA monolayer. The other two may provide additional attributes to the multilayer assembly (i.e. perspiration removal characteristics through the use of NOMEX or Gore-Tex).

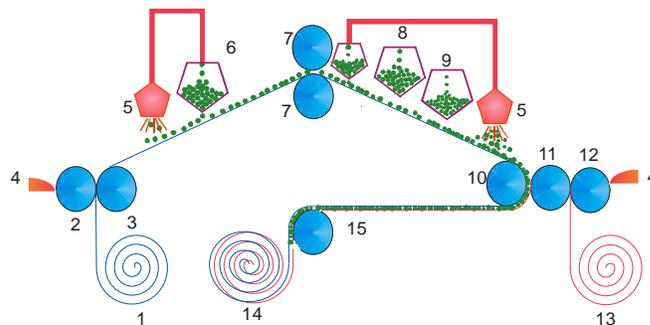


Figure 3. Schematic representation of the printing process and the pilot unit outlay.

The hot melt adhesives were applied on both the substrate and constraining layer during a two-stage process by means of a combination of a custom printing head and a hot melt extruder following a dot matrix pattern of 50-100 dots of adhesive per square inch (points 2 and 12). This was in accordance to the weave density of the substrate textile, while excessive amounts of adhesive were removed by a series of blades (point 4). A Kufner non-woven, thermo-adhesive Tech-Tex textile was used as the constraining layer (point 13). This was of sparse overall weave and exhibited a weight in the order of 40-50 gr/m². The SACA spherules were introduced to the substrate by means of a series of scales of various sizes (points 6, 8, 9) in a manner that ensured, uniform overall distribution of both particles as well as particles sizes. No sieves or similar methods for the distribution of spherules on the substrate fabric are used. As the use of sieves usually leads to blockage of the sieve holes and uneven distribution of the spherules, a different approach was applied. This involved the use of subsequent spherule drops from containers (points 6, 8, 9) containing spherules of the diameter. In this manner, the first stage of the spherule deposition is subsequently followed by additional drops. Every subsequent drop involves spherules of diameter approximately 1/3 of the diameter of the spherules deposited in the previous process step. As a measure towards the optimum allocations of spherules to all existing adhesive dots the spherules were forced into a rolling effect by means of a suitable angle that existed between the substrate textile and the horizontal and which was imposed by suitable positioning of the supportive textile rollers (points 10, 11, 15). In this manner, spherules introduced at different points during the deposition stage were allowed to roll and thus optimally occupy the available surface. However, the fact that the adhesive dot printing process created a two-dimensional uniformly spaced matrix of dots in conjunction to the fact that not all spherules were able to bond ideally (with respect to both the angle of the bond the percentage of the spherule surface attached to the adhesive dot lead to the formation of voids on the monolayer surface (Figures 3a and 3b).

A number of suction hoses were used for the removal of excessive spheroidal particles from the assembly (point 5) and a heated calender was used for the development of the monolayer. As an additional measure for the increase of the overall mechanical stability of the monolayer, the substrate and constraining layers were woven together.

For the adhesion of the SACA spherules to the carbon fabric a number of hot melt adhesives were utilized. Specifically, these included the National Starch PUR-FECT 310 or Henkel urethane hot melt). The hot melt adhesives were used, instead of "solid isocyanate" adhesives (such as the "high solids" Impranil-Imprafix of the Bayer company), which have been utilized and mentioned in a number of existing patents and licenses^[8], due to a number of disadvantages they pose. The basic disadvantage that has been explicitly presented both in previous relevant licenses and studies^[9] is that the hardening of "solid isocyanates" requires heating at 170 °C for 5 minutes. This renders necessary the addition of an extra step in the printing process and the integration of a heating oven. In a possible scale-up process of the currently presented pilot production unit this may imply significant costs in the production line development and subsequent operational costs. The pilot-unit assembly developed and presented in the current study is considerably simpler and involves lower development and operational costs. This may be attributed to the fact that the curing and hardening of the hot melt adhesives used takes place by means of adsorption of atmospheric humidity. The second important advantage of the utilization of humidity hardening hot melt adhesives is the increased resistance of the multilayer filter assembly in washing and similar cleaning processes.

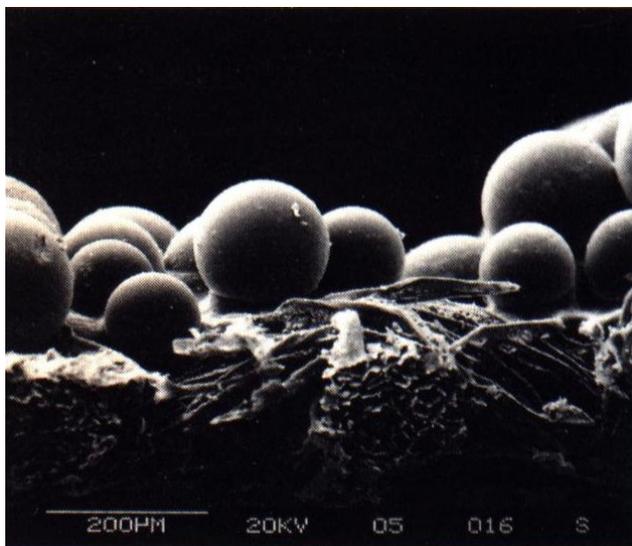


Figure 4a: Scanning Electron Microscopy micrograph of the printed SACA monolayer.

As the system, due to its increased mechanical attributes, is susceptible to further treatment for the improvement of both its physicochemical (i.e. adsorptive) as well as mechanical properties the treatment of the spherules with oxygen plasma will lead to the development of OH groups on the spherule surface, which will subsequently lead to the improvement of the morphology of the surface of spherules and the achievement of a significantly improved bond between the spherules and the adhesive as well as

to the development of a hydrophobic effect on the spherule surface.

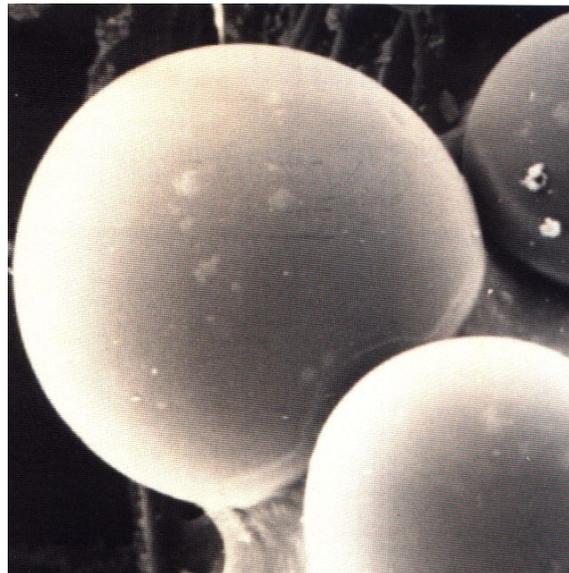


Figure 4b: Micrograph of the SACA-substrate interface and the adhesive dot.

4. Results

The results show that the SACA spherules prepared satisfactory physicochemical attributes that are suitable for their integration as an active monolayer into a multilayer assembly and the subsequent development of a filtering material system. The characterization of the SACA samples was carried-out by means of nitrogen porosimetry. The high surface area values which the prepared activated carbons present favor their utilization as adsorbents, while their impregnation with metals aims at attributing catalytic properties and selective adsorptive capability to these materials. After the verification of the necessary physicochemical and surface properties of the SACA materials the development of a pilot-unit and the optimization of a spherule printing process suitable for application in a pilot-scale production. Test runs that were carried-out indicated the soundness of the concept developed as well as its potential towards both optimized operation as well as scaling-up. The produced multilayer samples were primarily designed for use in bio-medical applications and for the development of suitable garments for hazardous environments. The increased levels of catalytic adsorption properties that were observed with respect to both gaseous and aqueous compounds and the bactericidal and bacteriostatic effects that were observed after application in biomedical applications (presented elsewhere) signify the potential of multilayer textile assemblies integrating a SACA active monolayer. Scale-up and process optimization studies are currently carried-out as well- as extensive characterization and process intensification efforts.

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