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The effect of gamma radiation on the properties of activated carbon cloth

DANIJELA R. SEKULIĆ, BILJANA M. BABIĆ, LJILJANA M. KLJAJEVIĆ, JELENA M. STAŠIĆ and BRANKA V. KALUDJEROVIĆ*

"Vinča" Institute of Nuclear Sciences, Laboratory for Materials Science, P.O. Box 522, 11001 Belgrade, Serbia

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Abstract: Activated carbon cloth dressing is an appropriate wound healing material due to its biocompatibility and adsorption characteristics. The influence of gamma radiation as a sterilization process on the adsorption and mechanical properties of activated carbon cloth was investigated. The specific surface area, micropore volume, pore size distribution, surface chemistry as well as the breaking load of activated carbon cloth before and after gamma radiation were examined. Characterization by nitrogen adsorption showed that the activated carbon cloth was a microporous material with a high specific surface area and micropores smaller than 1 nm. Gamma radiation decreased the specific surface area and micropore volume but increased the pore width. The sterilization process changed the surface chemistry quantitatively, but not qualitatively. In addition, the breaking load decreased but without any influence considering the further application of this material.

Keywords: activated carbon cloth; dressing material; gamma radiation; adsorption; surface modification.

INTRODUCTION

The potential of activated carbon cloth (ACC) in wound management relates to its ability to adsorb small gas molecules released from a wound, which are produced by anaerobic or proteolytic bacteria.[1–3] These molecules, which are responsible for the production of malodor, are attracted to the surface of the carbon and are held there by electrical forces.[4] This occurs due to the microporous structure of ACC consisting of thin slit-like pores that increase the effective surface area of the carbon fibers.[4,5] The ease of containment, formability, handling and especially the apparent biocompatibility are positive attributes and significant advantages for the application of ACC for dressings. The advantages of

* Corresponding author. E-mail: branka@vinca.rs
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activated carbon cloth over granulated active carbon or medical gauze are generally a higher pore volume (especially micropore volume) and surface area, which lead to a higher adsorption capacity and faster adsorption–desorption processes.[6] ACC appears to be useful for the adsorption of low and medium molecular weight organic compounds and bacteria.[3]

Such dressings can also be supports for therapeutic or antiseptic materials.[7] The disadvantage is that the agent incorporated into the dressing, inherently limits the bacteria-adsorbing characteristics of the carbon cloth and could adversely affect wound healing.

The adsorption capacity of ACC is controllable and depends on the raw material and the methods and conditions used in the production processes (carbonization and activation processes).[6,8–12] The pore size, specific surface area and surface chemistry of ACC significantly influence the adsorption capacity. For the adsorption of inorganic and polar organic molecules, both the porous structure and surface chemistry of the adsorbents are important. Carbon–oxygen surface structures, such as carboxyls, lactones, and phenols, are the most important ones affecting the surface characteristics and the properties of activated carbons. The activation is usually achieved by exposing a carbon material to an oxidizing gas, such as steam, air, CO_2, *etc*., or by mixing the precursor with oxidizing solutions. In addition, the exposure of carbon cloth to CO and CO_2 laser irradiation enhanced the content of surface oxygen complexes.[11] The surface chemistry of ACC can be modified using a microwave device as a heat source.[12]

The sterilization process of the examined ACC was performed by γ-radiation. Hence, it is important to determine whether the sterilization process influences the characteristics of the ACC. In this study, the influence of γ-radiation on the adsorption and mechanical characteristics of the ACC were examined.

EXPERIMENTAL

The viscose rayon cloth used as the carbon cloth precursor was soaked in an aqueous solution of a mixture of NH_4Cl and $ZnCl_2$ before the carbonization process. The carbonization process was performed in a nitrogen flow, which was followed by activation process in a CO_2 flow between 1123 K and 1273 K for 1 h. The ACC samples were washed in distilled water to remove traces of chlorides and other soluble impurities.

The samples were cut to a dressing form and wrapped in an aluminum package and sealed. These packages were then sterilized by γ-radiation. Packages were irradiated with a dose of 25 kGy over three days using a ^{60}Co-source.

The adsorption characteristics of the ACC were determined before and after γ-radiation by the standard N_2 adsorption technique at 77 K.[13] The adsorption and desorption isotherms of N_2 were determined gravimetrically using a McBain balance. From the adsorption isotherm, the specific surface area, S_{BET}, the total pore volume V_{tot}, the micropore volume, V_{mic}, the mesopores and macropores including the external surface area, S_{ext}, and the pore size distribution for the samples were calculated. The specific surface area, S_{BET}, was calculated using the Brunauer–Emmet–Teller (BET) method.[13] The total pore volume, V_t, was expressed

by the Gurwitsch rule using the quantity adsorbed (n) close to saturation, at a relative pressure $p/p_0 = 0.95$.[13] The Dubinin–Radushkevich (DR) equation was used to calculate the volume of the microspores (V_{micD-R}) of the ACC and the characteristic adsorption energy (E_0).[14]

The high resolution α_s-plot proposed by Kaneko *et al.*[15] was used to calculate the external surface area (S_{ext}), the total surface area (S_{tot}) and the micropore volume ($V_{mic\alpha}$). The micropore surface area, S_{mic}, was calculated by subtracting S_{ext} from S_{tot}.

The characteristic size of the slit-shaped pores is their average pore width (L_{sr}). The pore size distribution was estimated by applying the Horvath and Kawazoe (HK)[16] method and the numerical method of Pierce modified by Orr and Dalla Valle.[13] The HK method is valid for micropores (less than 2 nm) and the modified Pierce method for mesopores (over 2 nm).

The content of oxygen containing surface groups was investigated by the acid–base titration method proposed by Boehm.[17] The samples were contacted with 0.10 M $NaHCO_3$, 0.050 M Na_2CO_3 and 0.10 M NaOH solutions. After equilibration for at least 24 h, the excess of each base was estimated by titration with 0.10 M HCl using methyl orange as the indicator.

The breaking loads of the ACC before and after γ-radiation were measured with a Universal Testing Machine, model Instron 1185.

The morphological modification of the surface was examined by scanning electron microscopy (SEM) using a model JEOL-JSM-35 microscope.

RESULTS AND DISCUSSION

The adsorption characteristics of activated carbon cloth before (ACC) and after γ-radiation (ACCγ) are shown in Fig. 1 by the nitrogen adsorption and desorption isotherms at 77 K. These adsorption isotherms belong to type I isotherms according to IUPAC classification and indicate a microporous material.[18] Many type I isotherms exhibit no hysteresis at all, but the isotherms for ACC display a low pressure hysteresis and the isotherms for ACCγ display hysteresis over the whole range of measurement (Fig. 1).

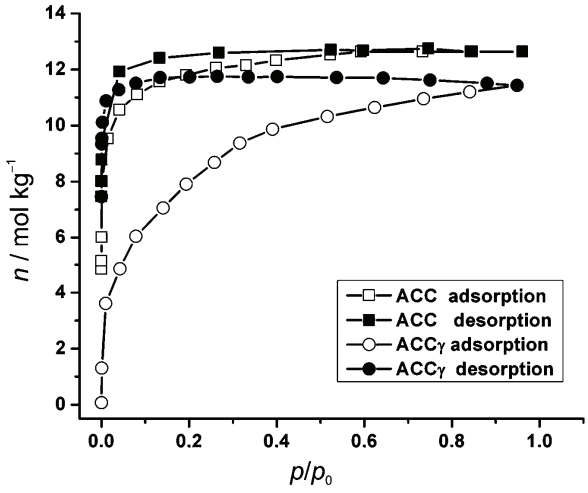


Fig. 1. Nitrogen adsorption/desorption isotherm at 77 K on activated carbon cloth before (ACC) and after γ-irradiation (ACCγ).

A hysteresis for a relative pressure higher than 0.4 indicates the presence of mesopores. On the other hand, low pressure hysteresis, when the relative pressure is lower than 0.4, means that some adsorbate is retained in the pores. The retained adsorbate persists after prolonged outgassing and can be removed only by pumping at elevated temperatures.

The knees of the nitrogen adsorption isotherms for ACC and ACCγ at 77 K are different (Fig. 1). In the case of adsorption by the ACC (sharp knee), the uptake reached a limiting value, manifested by the plateau in the adsorption isotherm. This means that the net heat of adsorption is high and the micropores are narrow. Slit pores with smaller widths are characterized by having greater adsorption energy due to the superposition of the adsorption potentials of the opposite pore walls. In addition, the plateau of the isotherm was nearly or completely horizontal, and the value of the microporous capacity was close to the uptake at saturation pressure.

When the knee of the isotherm is rounded, as was the case for the ACCγ isotherm (see Fig. 1), the net heat of adsorption is smaller and the micropores are wider. The value of the capacity of the micropores is hard to locate. Therefore, it is quite different from the value of the total capacity derived from the isotherm plateau, and even mesopores could be present. The presence of mesopores was confirmed by the existence of hysteresis (Fig. 1). These observations are quantitatively confirmed by analysis of the further experimental results.

TABLE I. Adsorption characteristics of ACC and ACCγ determined from BET, D–R and α_s-plots

Sample	S_{BET} m^2/g	V_t cm^3/g	V_{micD-R} cm^3/g	E_0 kJ/mol	$V_{mic\alpha}$ cm^3/g	S_{tot} m^2/g	S_{ext} m^2/g	S_{mic} m^2/g
ACC	985	0.438	0.393	23.75	0.378	1025	16	1009
ACCγ	668	0.396	0.263	12.59	0.325	884	76	808

The values of specific surface area (S_{BET} and S_{tot}), as well as S_{mic}, were higher for the ACC samples before γ-radiation (Table I). Moreover, the total pore volume V_t was higher before radiation. In addition, S_{ext} was 8.6 % of S_{tot} after the sterilization process, which is higher compared to the proportion of the external area to the total surface area of the starting material (1.6 %). This confirms formation of mesopores during γ-radiation. The values of the microporous volume were higher for the material before radiation, which is confirmed by calculations from both D–R and α_s-plots (Table I).

The values of V_{mic} obtained from these two methods are in disagreement, which was more pronounced for the ACCγ. The branch that corresponds to micropore filling in the D–R plot for ACCγ was not linear, which may cause the lower estimated value for $V_{mic\alpha}$ (Fig. 2). In addition, this could be a consequence of the broad size distribution of the micropores present in the ACCγ. This was con-

firmed by analysis of the pore size distribution (Fig. 3). The presence of mesopores (pores larger than 2 nm) in the ACCγ samples was also corroborated by this analysis.

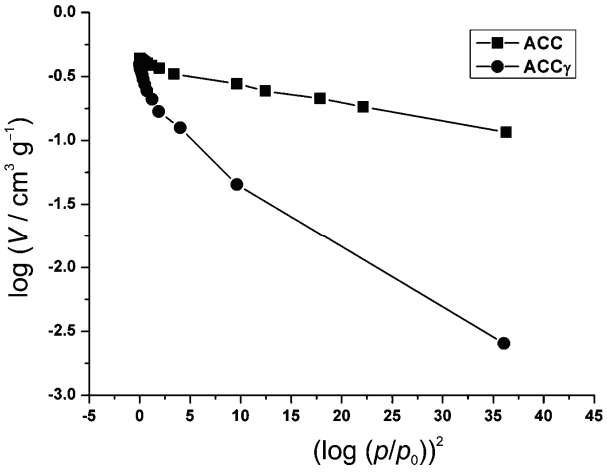


Fig. 2. D–R plots for nitrogen adsorption at 77 K on ACC and ACCγ.

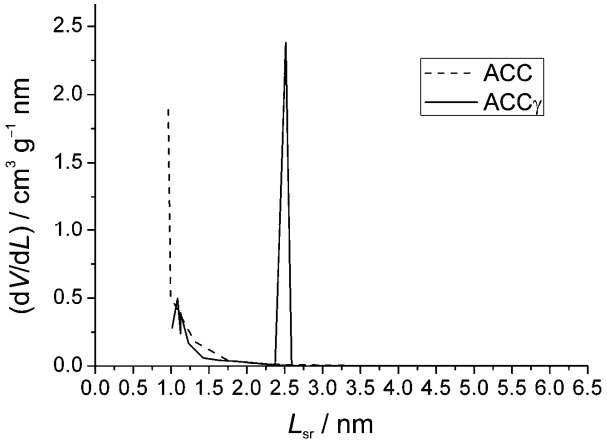


Fig. 3. Pore size distributions for ACC and ACCγ.

The size of the majority of the micropores in the ACC before γ-radiation was below 1 nm (Fig. 3). In such micropores, the mechanism of adsorption is pore filling rather than surface coverage explained by the D–R theory. Hence, the D–R plot, which describes the micropore filling of the ACC, is linear, as shown in Fig. 2. The D–R plot for the ACCγ deviated from linearity at low pressures. This arose from the overlap of the micropore filling process and multilayer adsorption, as a consequence of the broad distribution of pore sizes (Fig. 3). The micropore

volume decreased after the sterilization process. The characteristic energy of adsorption, E_0, also decreased, which indicates an increase in the pore size (Table I and Fig. 3).

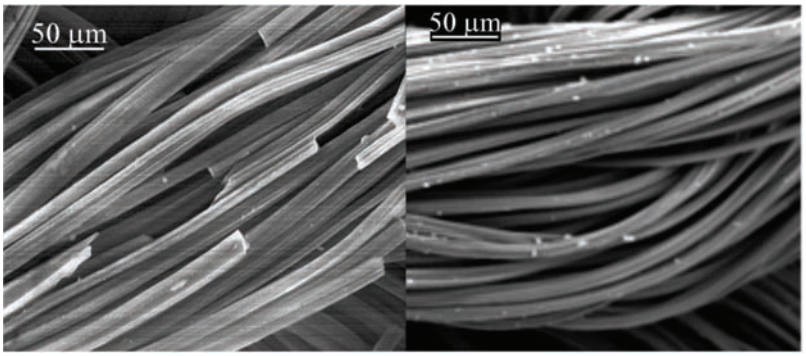
The α_s-analysis also indicated that the sterilization process induced changes in the porous structure. The micropore volume and the total surface area decreased, while the external surface area increased. The decrease of V_{mic} could be explained by changes in the pore size induced by γ-radiation, but the mechanism itself that induced the changes cannot.

TABLE II. Content of acidic oxygen-containing groups on the ACC and ACCγ surface

Sample	Total acidity mol/kg	Content, %		
		Phenolic groups	Lactonic groups	Carboxylic groups
ACC	8.8	41	17	42
ACCγ	12.8	43	16	41

The decrease of the total surface area could be provoked by the increase of the content functional groups on the surface after the sterilization process (Table II). These groups occupied sites at the edges of the pores and in that way decreased surface area.[6] It can be seen that the content of each group remained the same but the total acidity increased. The small amount of air remaining in the sealed ACC packages, together with the high energy of γ-radiation, was sufficient to induce the formation of oxygen-containing groups in the ACCγ.

The breaking load (the maximum load that the specimen can tolerate without breaking) of the ACC was slightly decreased after γ-irradiation, from 21 to 18 N. This behavior was expected – the wider the pores are, the smaller is the break resistance of the cloth. In addition, sporadic fiber damage is induced by γ-irradiation, especially on the side directly exposed to the radiation, which can be seen in the SEM microphotographs of the ACCγ shown in Fig. 4.



(a) (b)

Fig. 4. SEM Microphotographs of ACCγ from: a) side directly exposed to the γ-radiation; b) the opposite side.

CONCLUSIONS

Due to its biocompatibility and developed adsorption characteristics, ACC could be used as a dressing material for healing wounds even without drugs. For this purpose, the influence of ACC irradiation by γ rays on the adsorption and mechanical properties of the activated carbon cloth was examined.

Gamma radiation induced pore widening and the formation of mesopores in the material, which provoked a broad distribution of the pore sizes. These changes promote the retention of adsorbates in the pores and make the material more convenient for further application as a dressing or as a filter material.

Although the content of functional groups after gamma radiation of the ACC remained the same, the total acidity was increased. This induced a decrease of the specific surface area, which was nevertheless still high. Functional groups on the ACC surface, as well as a high surface area, are very important for the adsorption of inorganic and polar organic molecules.

The decrease in the mechanical properties of the ACC after gamma radiation was not so drastic as to make them inappropriate for their future usage.

The obtained results suggest that gamma-irradiation is a suitable technique for the sterilization of activated carbon cloth.

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И З В О Д

УТИЦАЈ ГАМА ЗРАЧЕЊА НА СВОЈСТВА АКТИВНЕ УГЉЕНИЧНЕ ТКАНИНЕ

ДАНИЈЕЛА П. СЕКУЛИЋ, БИЉАНА М. БАБИЋ, ЉИЉАНА М. КЉАЈЕВИЋ,
ЈЕЛЕНА М. СТАШИЋ и БРАНКА В. КАЛУЂЕРОВИЋ

Институт за нуклеарне науке "Винча", Лабораторија за материјале, п. пр. 522, 11001 Београд

Захваљујући биокомпатибилности и адсорпционим својствима, завоји од активног угљеничног материјала су врло погодни за лечење рана. Испитиван је утицај процеса стерилизације гама зрачењем на адсорпциона и механичка својства активне угљеничне тканине. Специфична површина, запремина микропора, расподела величине пора, хемија површине, као и прекидна сила, су одређиване пре и после гама зрачења. Карактеризација материјала помоћу адсорпције азота је показала да је активна угљенична тканина микропорозна, велике специфичне површине са микропорама мањим од 1 nm. Гама зрачење смањује специфичну површину и запремину микропора, а повећава ширину пора. Процес стерилизације мења хемију површине квантитативно, али не и квалитативно. Такође се смањује и прекидна сила, али без неког утицаја за даљу примену материјала.

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