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CARBON FIBERS AND TEXTILES AND SOME OF THEIR APPLICATIONS

Production process and characteristics of PAN based carbon fibers and cellulose based carbon textile are presented.

In the case of carbon fibers attention is payed to changes during the carbonization process in the range of 400–1000°C. The change of diameter and weight loss as well as tensile strength and Young's modulus were examined.

For carbon textile it was interesting to show their adsorption characteristics as activated material. The nitrogen adsorption isotherms correspond to the microporous adsorbent which is suitable for adsorption of both gaseous and liquid adsorbats.

Carbon fibers have been known since the end of the XIXth century, when Edison first produced filament for electric lamps by cellulose pyrolysis. From the middle of the last century till today interest in carbon fibers and other carbon materials, and their field of application are expanding.

Early on it was known that polymer fibers, mostly cellulose (especially rayon or viscose) fibers or polyacrylonitrile (PAN) fibers are good precursors for the production of carbon fibers. But, it is not necessary to choose polymer and textile fibers as the starting material. Otani was the first to show that it was possible to produce isotropic carbon fibers from molten pyrolysis products such as polyvinyl(chloride)pitch and coal tar pitch [1]. Fibers derived from other pitches – petroleum and coal tar, are now made commercially.

Yamada first succeeded in making glassy carbon filaments from a complex phenolic resin [2].

Also, it is possible to produce carbon fibers from gases such as hydrocarbons and organic compounds of transition metals, but in the form of segments of 0,05 μm to 30 cm [3–6].

Various classifications of carbon fibers result from their performance or their application. Thus, the classification by raw materials is cellulose-based fibers, PAN-based fibers, pitch-based mesophase fibers, lignin-based fibers and gas phase production fibers. If the textile form is considered, there are continuous filament yarn, stapel fibers, tows, textiles of various fabrics, ribbon yarn, felts, mats.

Some carbon fiber classifications are based on the final heat treatment temperature (HTT) during the pyrolysis of organic raw materials in the carbon fiber production process.

With the HTT increases, the carbon content in the fibers increase. So, carbon fibers may be divided into three groups:

- partially carbonized fibers (HTT 500°C, carbon content up to 90 wt.%);
- carbonized fibers (HTT 500–1500°C, carbon content 91–99 wt.%);
- graphitized fibers (HTT 2000–3000°C, carbon content over 99 wt.%).

The HTT of carbon fibers and raw materials are related to their physical and mechanical properties. The most general classification, on the basis of their mechanical properties, is:

- high modulus high tensile (HMT, Young's modulus (M) = 400–450 GPa, tensile strength (T) = 1700–2500 MPa);
- high modulus (HM, M = 300–700 GPa, T = 2000–2500 MPa);
- high tensile (HT, M = 200–250 GPa, T = 2500–3200 MPa);
- low modulus (LM, M = 50–150 GPa, T = 500 MPa).

Japanese researchers accept the physical approach to classification and have divided carbon fibers into high quality fibers and low quality (low grade) ones. High quality, PAN-based fibers, are classified into:

- high strength carbon fibers;
- high modulus graphite fibers;
- carbon fibers with enhanced strength and elasticity.

The (b) group can be produced using both PAN and mesophase pitch as the starting materials.

Depending on the desired properties of the article to be manufactured, various types of carbon fibers may be used. The application of carbon fibers of high performances is still limited by their high costs and their practical uses are limited to those applications where their employment will ensure better performance in comparison to conventional construction materials such as high mechanical stress, enhanced temperatures and

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radiation exposure. The preferred application area of high strength and high modulus carbon fibers is for producing composite materials with polymer or carbon matrices. These fibers enter as basic elements of construction materials in aerospace vehicles, in the aviation industry, technological engineering and the manufacturing of high quality sports gear and prostheses, etc. These composites successfully substitute metals and alloys, especially under extreme conditions.

The production of low modulus carbon fibers has increased. Their production technology is simpler and the raw material is abundant so, they are much cheaper. Owing to the versatility of fiber properties, high surface reactivity and lower overall costs, low modulus fibers have found effective application in various fields of application such as heat insulating shields, filtering and or sorption layers and coatings, as well as composites and electrically conducting materials, etc.

Also cellulose or PAN, cloth, cord and felt may be carbonized directly to carbon cloth, cord and felt. Such materials are manufactured for use as filters, catalyst carriers and thermal insulation.

In the Materials Laboratory at the Vinča Institute, work in the field of PAN based carbon fibers began in 1972, and in the field of cellulose based carbon textile in 1977 [7,8]. Some recent results are presented here.

PAN BASED CARBON FIBERS

At present polyacrylonitrile (PAN) is the main raw material for producing high strength and high modulus carbon fibers that are further used in manufacturing carbon plastics with high mechanical characteristics. The heat treatment temperatures for such fibers are usually below 1000°C, which explains why PAN – based fibers contain a considerable amount of bound nitrogen (up to 6 wt.%).

The process of producing PAN-based carbon fibers includes two principle stages: stabilization and carbonization. The stabilization of PAN-based fibers is frequently conducted by heating in oxidative media (air, oxygen, and oxygen mixtures with inert gases) at temperatures up to 350°C. At this stage the formation of chain ring structures takes place, which increases the thermal stability of the macromolecules and the solidity of the polymer. The PAN stabilization process includes, along with reactions leading to the binding of oxygen, cyclization and dehydration reactions. H₂O, NH₃ and HCN represent the volatiles. Thermal oxidation is accompanied by shrinkage of the fiber, the extent of which depends on the heating rates. On the basis DSC analysis it was concluded that two shrinkage mechanisms exist. Low-temperature shrinkage (corresponding to the 120°C maximum) is of a physical nature and its dependence on the heating rate is weak. Chemical shrinkage takes place at temperatures above

200°C at which cyclization processes take place with intramolecular cyclization occurring first. Chemical shrinkage depends on the conditions of thermal oxidation and affects on the characteristics of carbon fibers formed during subsequent stages. Stretching during thermal oxidation prevents shrinkage and represents an important stabilization condition, which ensures the production of carbon fibers with good characteristics. The carbonization of stabilized fibers results in gradual cross-linking of the chains, aromatization and, finally, to the formation of graphite-like structural elements. The mechanical properties of the final products depend on the dynamics of gas evolution.

The evolution of HCN takes place within two temperature ranges: 250–500°C and 700–1000°C. The low-temperature evolution of HCN is connected to intramolecular rearrangements and results in the formation of C=C bonds. The formation of HCN during the second stage is due to intermolecular interactions of the cyclic chains and results in formation of ordered graphite-like structures. Ammonia is removed in the 400–500°C range. Elementary nitrogen begins to evolve at temperatures above 600–700°C and it is accompanied by the formation of graphite like structures. Intermolecular linking of the cyclic chains also proceeds through the removal of oxygen-containing functional groups.

The mechanical characteristics of carbon fibers represent a very important indication of their quality. Young's modulus and the tensile strength depend on the direction of the applied stress. Usually, when describing the properties of carbon fibers, data on the strength and Young's modulus are ascribed to the direction along the fiber axis. The mechanical properties of carbon fibers are primarily determined by structural features of the fiber and depend largely upon the fiber structure developed at different stages of their production, on the presence of impurities, and various flaws. Changes in Young's modulus correlate with the degree of orientation in the carbon fiber, while the fiber tensile strength depends primarily on the structural defects.

An examination of the possibility of using PCF as reinforced materials instead of carbon fibers in production of carbon-carbon composites is presented in this study. As measure for comparable PFC and CF was applied a value of mechanical properties [9].

CELLULOSE BASED CARBON TEXTILE MATERIALS

The most popular application of carbon textile material is for filtering and or sorption layers, i.e. as adsorptive materials. To improve their characteristics to this aim it is necessary to develop microporosity by oxidation treatment. This is an activation process and carbon activated carbon.

Activated carbon cloth may be obtained by the carbonization and activation of previously impregnated cellulose. The impregnation process is necessary for improving the carbon yield during the carbonization of cellulose. Due to the high specific surface area and microporosity, activated carbon cloth shows good adsorptive properties both in the gaseous and the liquid phase [10].

Besides surface area and microporosity to improve adsorption from the gaseous phase, for some specific adsorbates it is sometimes necessary to impregnate activated carbon cloth with specific impregnants depending on the adsorbate.

In the case of adsorption from the liquid phase there is a strong dependence of adsorption on the pH and concentration of the solutions, the nature of the carbon surface and the size and shape of the pores in the adsorbent.

EXPERIMENTAL

Polyacrylonitrile (PAN) fibers (Hysol–Grafil) were used as raw materials for obtaining partially carbonized fibers (PCF). The process of making PCF consists of two phases: stabilization of the initial PAN fibers and partial carbonization of the stabilized fibers. These phases were carried out continuously in an experimental pilot plant which was constructed and modified the "Vinča" Institute. The stabilization process of PAN fibers was carried out in two steps. In the first step PAN fibers were heated up to 200°C at 9 °/min, and stretched 15% compared to their original length. In the second step the fibers were heated from 200°C to 280°C at 2 °/min and their length kept constant. The PAN fibers were carbonized to different temperatures (400, 500, 600, 700, 800, 900, 1000°C) at constant length in inert atmosphere. The mechanical characteristics of the initial, oxidized PAN fibers and PCF were investigated on a universal machine for examining of materials INSTRON 1185 by the stretching test, based on the ASTM D3379 standard. Based on these results, the tensile strength, and Young's modulus were determined.

The gauge length of the fibers was 30 mm. The diameter of a single filament was determined by optical microscopy. The diameter of the fibers represents the mean value of twenty measurements.

Viscose rayon cloth (Viskoza–Loznica) was used as a carbon precursor. The cloth was carbonized in a nitrogen flow and activated in carbon-dioxide flow at 850°C to obtain different activities.

Impregnation of the activated cloth was performed in a 10% aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 20% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 7% H_2SO_4 , to obtain equal salt contents of about 25% after drying.

The specific surface area and porous structure parameters were determined from N_2 adsorption isotherms at 77K using the gravimetric McBain method.

Amonia adsorption was measured at 303 K using the same adsorption method.

Initial pH values were obtained by adding an amount of KOH or HNO_3 solution (0.1 mol/dm^3), keeping the ionic strength constant. The amount of H^+ or OH^- ions adsorbed on activated carbon cloth was calculated from the difference between the initial and the final concentration of H^+ or OH^- ions.

The specific adsorption of counter ions was investigated using $1 \times 10^{-3} \text{ mol/dm}^3$ solutions of $\text{Zn}(\text{NO}_3)_2$ or $\text{Cd}(\text{NO}_3)_2$ of p.a. quality (Barič).

RESULTS AND DISCUSSION

The changes of the fiber diameter during the process of partial carbonization are shown in Figure 1. During the process of carbonization the fiber diameters was reduced, so that fibers carbonized up to 1000°C show radial shrinkage by 39% compared to initial values.

Figure 2 represents the mass changes of PAN oxidized fibers with temperature. The largest weight loss was observed in the temperature range from 600 to 800°C. In range 900–1000°C the weight of PCF was

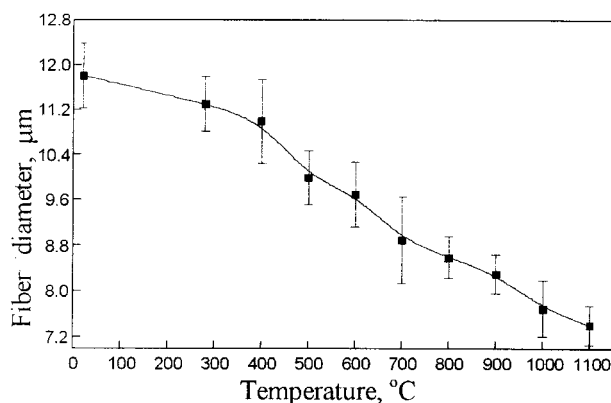


Figure 1. Changes in the fiber diameter during the partial carbonization process

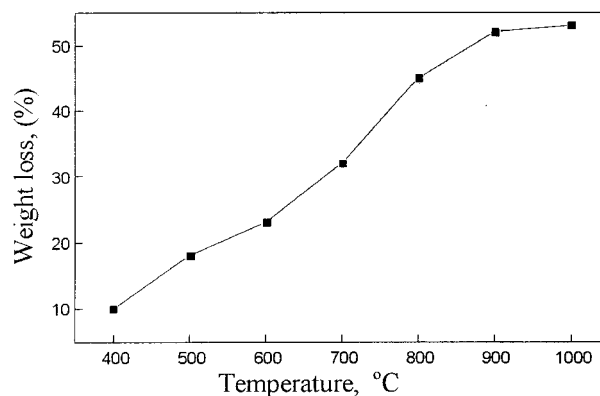


Figure 2. Weight loss of fibers during the partial carbonization process

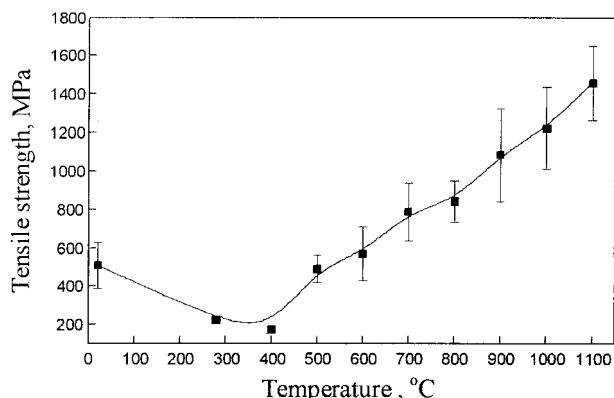


Figure 3. Dependence of tensile strength on the carbonization temperature

decreased, by 1.9 wt.%. Nitrogen began to evolve at 700°C and reached a maximum at 900°C. The chemical reactions of carbonization are fundamentally irreversible reactions of pyrolysis during which almost every element evaporates in the form of gaseous products except carbon.

Because of the present defects in the fiber structure, considerable dispersion of the results was observed especially regarding the strength. Figure 3 represents the fiber tensile strength as a function of the carbonization temperatures. It was observed that the initial PAN fibers were stronger than the oxidized fibers. In the initial carbonization phases the tensile strength decreased and at 400°C reacted minimum values and in subsequent steps grew almost linearly.

Young's modulus is one of the most important mechanical properties of carbon fibers. Figure 4 represents the Young modulus as a function of temperature and it increases linearly with carbonization temperature. This is necessary to order the graphite structure gradually.

The nitrogen adsorption isotherms presented in Figure 5 for activated samples of different activity are of

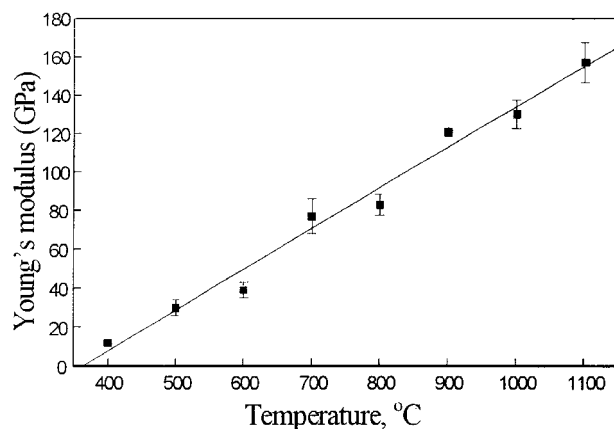


Figure 4. Dependence of Young's modulus on the carbonization temperature

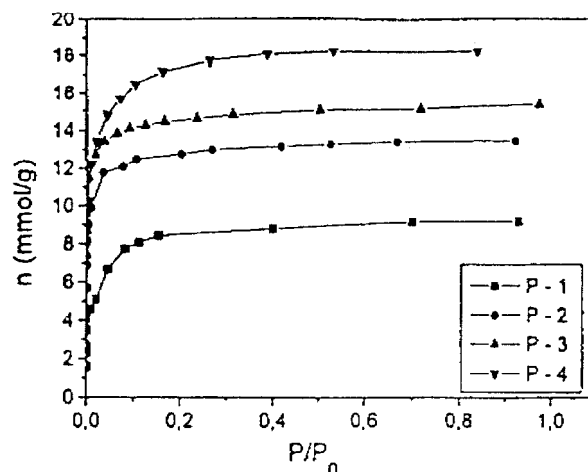


Figure 5. Nitrogen adsorption isotherms (77K) for activated carbon cloth

Table 1. Nitrogen adsorption data (77 K) for activated carbon cloth

Sample	A-BET m ² /g	A _{ext-αs} m ² /g	V-α _s cm ³ /g	E ₀ -DR kJ/mol	W _m -DR nm
P-1	720	0.07	0.30	16.9	1.52
P-2	1080	0.50	0.46	18.6	1.36
P-3	1243	0.77	0.51	22.6	1.04
P-4	1411	0.65	0.62	17.6	1.45
P-4 + H ₂ SO ₄	875	0.52	0.32	17.2	1.48
P-4 + CuCl ₂	968	0.58	0.41	20.8	1.17

type I. The curve shapes are typical for microporous carbon.

The porous structure parameters are given in Table 1. The BET method was used to calculate the specific surface area. The external area surface A_{ext-αs} and micropore volume V-α_s were calculated from the slope and intercept of the linear part of the α_s curve. The nitrogen adsorption data for olive stone activated carbon was used as the reference data. DR plots were used to obtain the micropore volume and the characteristic adsorption energy E₀, which was used for calculating the micropore sizes.

The data presented in Table 1 show that, the specific surface area and micropore volume also increase with increasing activity from samples P-1 to P-4.

The high values of the adsorption energy E₀ and small values for the non-microporous surface area A_{ext} are a consequence of the dominant microporous structure.

The salts introduced by impregnation filled the micropores of the activated carbon cloth, leading to a decrease of the specific surface area and pore volume.

The adsorption isotherms for ammonia are presented in Figures 6 and 7.

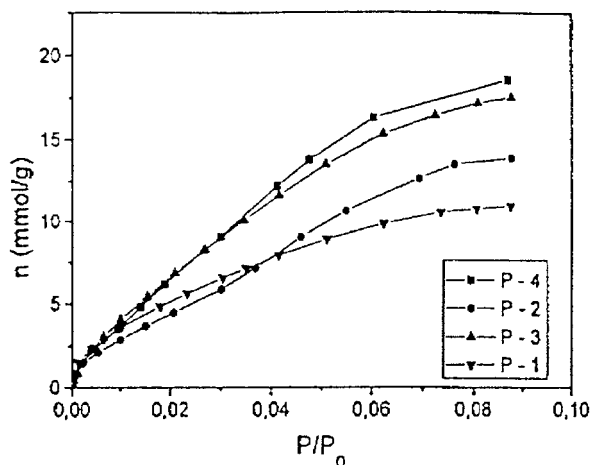


Figure 6. Ammonia adsorption isotherms (303K) for activated carbon cloth with various activity

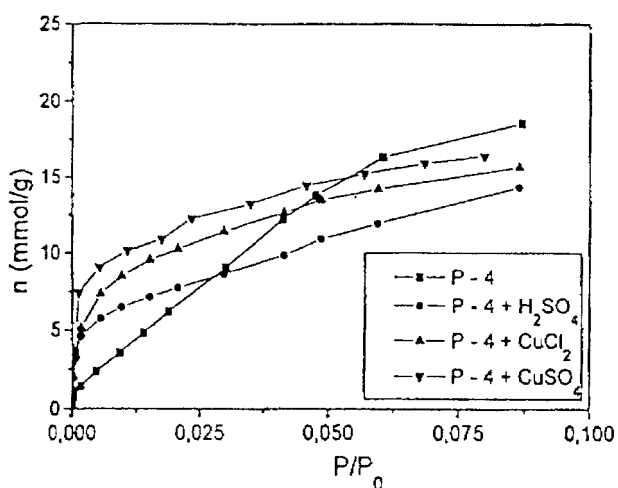


Figure 7. Ammonia adsorption isotherms for impregnated active carbon cloth

The adsorption activity at high relative pressures of NH_3 increased with increasing surface area and micropore volume (see Figure 6).

The influence of impregnation on the increase of the adsorption efficiency at low NH_3 concentrations is evident from Figure 7.

The adsorption of Zn^{2+} and Cd^{2+} ions from aqueous solutions as a function of pH values are presented in Figures 8 and 9.

In both cases ion adsorption increases with increasing pH. The isotherm curves are complex because of the simultaneous influence of the metal ion concentration.

CONCLUSION

The mechanical properties of PCF (400–1000°C) produced from PAN fibers as a precursor, were investigated. On the basis of the values of weight loss for fibers which were carbonized to 1000°C (53%) it was

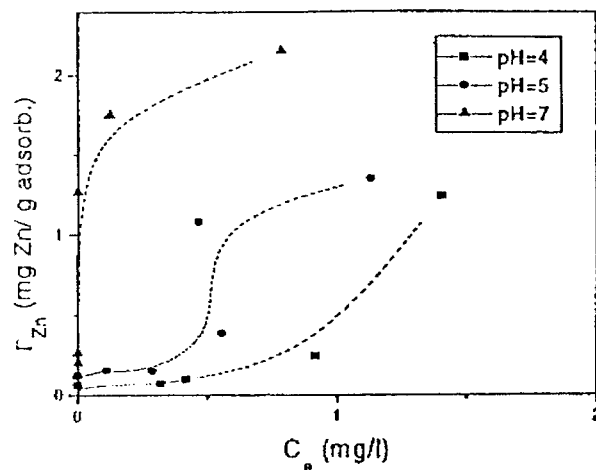


Figure 8. Zinc adsorption isotherms for different pH values

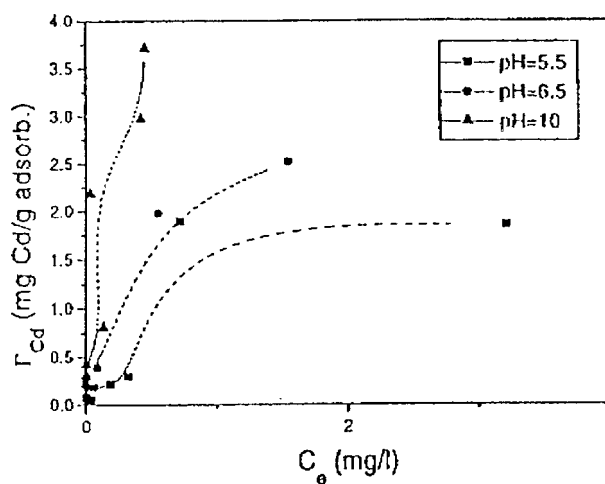


Figure 9. Cadmium adsorption isotherms for different pH values

concluded that most non-carbon elements were eliminated in the form of gaseous products.

The increase of the value of the tensile strength is gradual above 400°C. The Young modulus of PCF increases linearly with temperature.

Activated carbon cloth can be successfully applied in the field of gaseous and liquid pollutant adsorption.

The sorbent properties depend on the surface characteristics, microporosity of the adsorbents and in the case of aqueous solutions on the pH values.

The adsorption properties may be improved by impregnation of the activated materials.

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IZVOD

UGLJENIČNA VLAKNA, TEKSTIL I NEKE OD NJIHOVIH PRIMENA

(Naučni rad)

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Proces proizvodnje i karakteristike ugljeničnih vlakana na bazi PAN-a i ugljeničnog tekstila na bazi celuloze su dati generalno.

Kod ugljeničnih vlakana prikazane su promene koje se javljaju u procesu karbonizacije. Za opseg temperatura od 400–1000°C praćene su promene prečnika i gubitak mase kao i zatezna čvrstoća i Young-ov modul.

Kod ugljeničnih tekstila prikazane su njihove adsorpcione karakteristike kao aktivnog materijala. Adsorpcija azota pod izotermnim uslovima ukazuje na mikroporozni adsorbens, pogodan za adsorpciju i gasnog i tečnog adsorbata.

Ključne reči: Parcijalna karbonizovana vlakna • Ugljenična tkanina • Mehanička svojstva • Adsorpciona svojstva •

Key words: Partially carbonized fibers • Carbon cloth • Mechanical properties • Adsorption characteristics •