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Functionalization methods of carbon fibers – an overview

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Abstract: This article is a literature review related to the methods of functionalization of carbon fibers for tissue engineering applications. Through physical modification, it is possible to obtain a layer of a chemical compound on the carbon fibers surface and to impart additional properties. On the other hand, chemical modification may lead to the incorporation of appropriate functional groups into the carbon fiber structure, capable of attaching, among others, biologically active compounds. The paper presents the advantages and disadvantages of the carbon fibers modifying methods, with particular emphasis on the use of such modified fibers in medicine.

Keywords: carbon fiber, functionalization, dip-coating.

Metody funkcjonalizacji powierzchni włókien węglowych – przegląd literaturowy

Streszczenie: Niniejsza praca stanowi przegląd literatury dotyczący metod funkcjonalizacji włókien węglowych przeznaczonych do zastosowań w inżynierii tkankowej. Poprzez modyfikację fizyczną możliwe jest uzyskanie warstwy związku chemicznego na powierzchni włókien węglowych i nadanie im dodatkowych właściwości. Natomiast modyfikacja chemiczna może prowadzić do wbudowania w strukturę włókna węglowego odpowiednich grup funkcyjnych zdolnych do przyłączania m.in. związków aktywnych biologicznie. W pracy przedstawiono zalety i wady stosowanych metod modyfikacji włókien węglowych, ze szczególnym naciskiem na zastosowanie tak modyfikowanych włókien w medycynie.

Słowa kluczowe: włókno węglowe, funkcjonalizacja, powlekanie zanurzeniowe.

Carbon fiber (CF) is a material included in both fibrous materials, as well as carbon materials. It is characterized by high carbon contents (above 92% parts by weight) [1]. Likewise, the other fibrous materials, carbon fibers are produced in continuous or segmented form. Carbon fibers are most often used as reinforcements for polymer composites, which is explained by the fact that they have a high specific modulus and specific strength, among the commercially used reinforcing fibers. In addition, carbon fibers have satisfactory thermal and chemical resistance, and their properties remain unchanged in non-oxidizing environment, up to 2000°C [2]. They are also characterized by low density, good thermal and electrical conductivity, low coefficient of friction and the ability to absorb vibrations [3]. These characteristics have resulted in specific applications of carbon fibers in various fields of the

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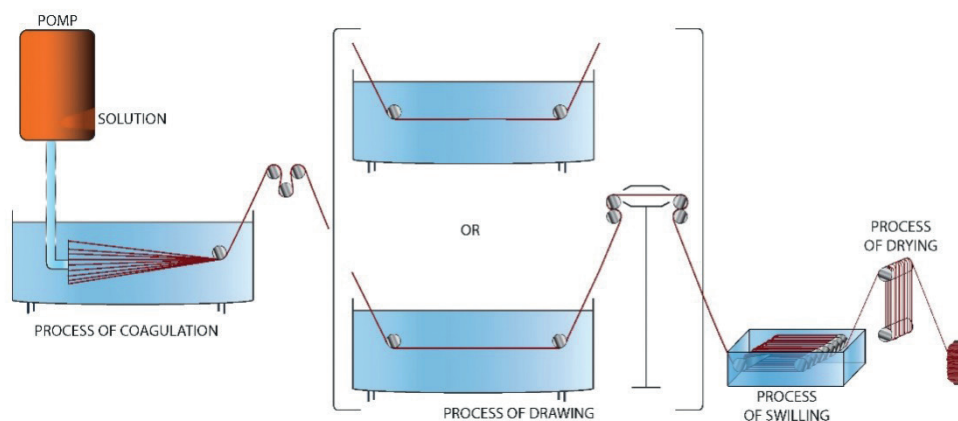
Fig. 1. Scheme of the process of manufacturing PAN fibers by wet spinning

economy, including: construction (improving the load-
-bearing capacity of bridge structures) [4], production
of sports accessories (golf poles, tennis racquets, arrows
for archers) [5], construction of racing cars [6], aerospace
constructions (helicopter blades, pressure vessels, engine
components) [2,7] and in medical applications [8].

Such extensive use of carbon fibers would not be possi-
ble without pre-functionalization of their surfaces, inten-
ded to reduce their hydrophobicity. The hydrophobi-
city of carbon fibers results in low adhesion to polymer
matrices [9]. The use of CFs with untreated surface gives
a composite with low compressive strength. Surface tre-
atment of CFs may reduce or eliminate this problem. By
using pre-treatment processes, the content of carboxyl
groups on the CF surface is increased, the wettability of
the fibers and their compressive strength are improved,
the hydrophilicity of the surface is increased [10], resul-
ting in a material significantly more useful for materials
engineering. This paper is a mini review of the literature
on the modification of carbon fibers.

CARBON FIBERS - STRUCTURE, MANUFACTURING AND PHYSICOCHEMICAL PROPERTIES

Chemical structure and manufacturing process of carbon fibers

Several methods are known for obtaining carbon fibers
from various raw materials, which include carbon gases
(such as acetylene), pitch fibers and polymer fibers (poly-
acrylonitrile, viscose and others). Considering the eco-
nomic aspect (cost of raw materials), it is more advan-
tageous to obtain carbon fibers from carbon pitch and
gases. However, the most widely used method for obta-
ining carbon fibers is the one using polymers as sub-
strates. Due to the properties of the obtained fibers [11],
90% of the world's carbon fiber production, is based on
the use of polyacrylonitrile (PAN) fibers as a precursor.
Carbon fibers from PAN precursor show more favorable
mechanical properties than those produced from other
types of precursors. This manufacturing method has

a higher carbon capacity (>50% of the weight of the pre-
cursor used) than with other types of fibers. The process
of manufacturing CF from PAN precursor is a multi-step
process and includes:

– polymerization of polyacrylonitrile,
– wet spinning (Fig. 1),
– stabilization in an oxidizing atmosphere,
– carbonization in an ambience atmosphere,
– optionally – graphitization process.

In the first step, the acrylonitrile monomer CH_2=CH–
CN undergoes polymerization. Then, the resulting poly-
mer is dissolved (DMF, NaCNS) and extruded through
the spinning nozzle into the coagulation bath, where the
fiber structure is solidified. When forming this type of
fiber, there is a two-way mass exchange. The medium,
which is the insolvent, enters the stream of spinning solu-
tion from the coagulation bath, while the solvent from the
solution passes into the coagulation bath. The ratio of the
solvent to non-solvent stream is extremely important, as
the cross-sectional area of the finally formed fibers, lar-
gely depends on it. As a result of this process, the polymer
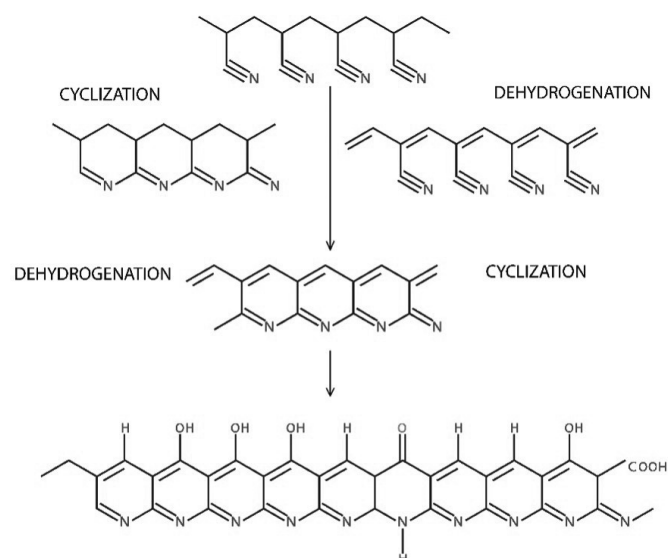stream solidifies and a freshly solidified fiber is formed,

**Fig. 2. Sequence of the reactions occurring in the process of ther-
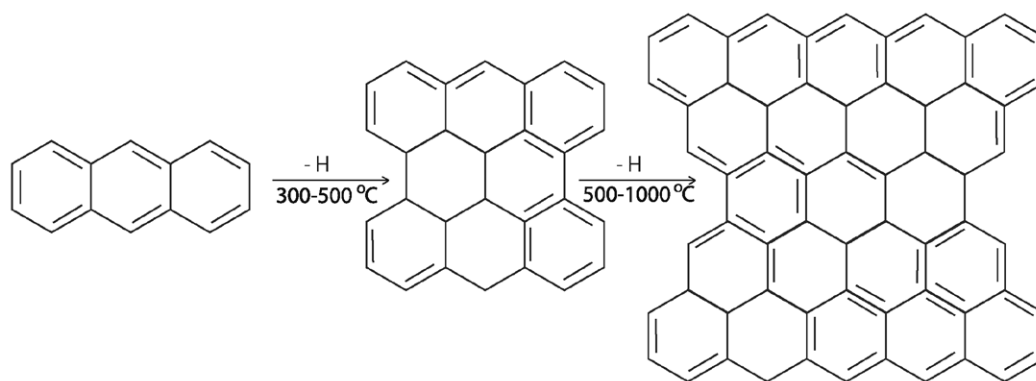mo-oxidative stabilization of PAN**

Fig. 3. General scheme of carbonization reaction of carbon fibers

which undergoes orientation in subsequent stages of the technological process (drawing process). The fibers are then washed and dried under isometric conditions.

The obtained precursor fibers are subjected to further thermal treatment processes to obtain the carbon structure. The first step is to stabilize the fibers by performing the following reactions: cyclization, dehydrogenation and oxidation (Fig. 2) [11].

The next stage involves the process of the fiber's carbonization, which involves exposure to high temperatures (400–1500°C) in an atmosphere of inert gas, most often argon (Fig. 3).

The parameters of the carbonization process directly affect both the porosity of the resulting carbon fiber's structure and their mechanical properties (*e.g.*, tensile strength).

Physicochemical properties of carbon fibers

The chemical structure of the fibres, as well as their manufacturing process, affect the final properties and application area. Based on the way in which crystallites are oriented in the fibres, as well as their mechanical properties, carbon fibres are divided into ultra-high modulus (UHM), high modulus (HM), intermediate modulus (IM), standard modulus (HT) and low modulus (LM) [11] (Table 1).

UHM and HM carbon fibres undergo efficient graphitization in the range of temperatures 2000–3000°C and are characterized by a high coefficient of elasticity (>350 GPa). Sometimes they are even defined as high-modulus Type I carbon fibres. Type II carbon fibres (which inc-

lude IM and HT carbon fibres) are called high-strength but low-modulus fibres because of the lower heat-treatment temperature (~1500–2000°C). Their tensile stress can be bigger than 3 GPa, and a strength-to-modulus ratio bigger than 1×10^{-2}. Type III carbon fibres include fibres with disordered (random) orientation of crystallites. These fibres have a modulus of less than 100 GPa.

Carbon fibers can also be classified based on their commercial availability. A classification is made between the following fibers: high-performance (HP), general-purpose (GP), and activated (ACF). General-purpose carbon fibers have low tensile stress and low elastic coefficient but are the most economical to produce. HP carbon fibers have very high mechanical strength and high elastic coefficient due to their higher graphite content and higher anisotropy. These features make such fibers widely used as reinforcement for polymer composites (CFRP) used in the aerospace industry. ACFs are carbon fibers with a high specific surface area and micro-pores volume, which are used mainly as adsorbents, membranes for separation and purification, and catalyst carriers.

METHODS OF SURFACE FUNCTIONALIZATION OF THE CARBON FIBERS

The primary goal of carbon fibers surface functionalization is to improve their mechanical properties, abrasion resistance and simplification of their processing in the textile industry (weaving or spinning). CF surface modifications affect the fiber structure and the strength of chemical bonds to the composite matrix. Surface treatment

T a b l e 1. Classification and properties of carbon fibers [11]

Class of the carbon fibers	Coefficient of elasticity by the tension, GPa	Tensile strength MPa	Temperature of heat treating °C	Crystal orientation
Ultra-high modulus (UHM)	≥ 600	≥ 2500	~ 2000–3000	Largely parallel to the fiber axis
High modulus (HM)	350–600	≥ 2500	~ 2000–3000	Largely parallel to the fiber axis
Intermediate modulus (IM)	280–350	≥ 3500	~ 1500–2000	Largely parallel to the fiber axis
Standard modulus (HT)	200–280	≥ 2500	~ 1500	Largely parallel to the fiber axis
Low modulus (LM)	≤ 200	≤ 3500	~ 1000	Random

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┌─────────────────────┐                          ┌─────────────────────┐
│ Oxidative treatment │                          │    Non-oxidative    │
│                     │                          │      treatment      │
└─────────────────────┘                          └─────────────────────┘
        │                                                 │
        ├──┌─────────────────────┐                        ├──┌─────────────────────┐
        │  │  Gas-phase oxidation │                        │  │ High-efficient shaking │
        │  └─────────────────────┘                        │  └─────────────────────┘
        │                                                 │
        ├──┌─────────────────────┐                        ├──┌─────────────────────┐
        │  │ Liquid-phase oxidation │                      │  │ Deposition of pyroliitic carbon │
        │  └─────────────────────┘                        │  └─────────────────────┘
        │                                                 │
        └──┌─────────────────────┐                        └──┌─────────────────────┐
           │  Catalytic oxidation │                          │ Graphitization of polymers │
           └─────────────────────┘                          │      on the surface      │
                                                            └─────────────────────┘
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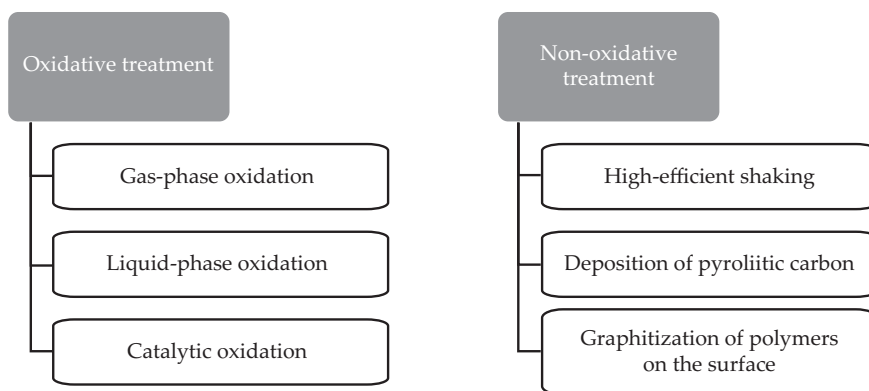
Fig. 4. Functionalization methods of carbon fibers' surface

of carbon fibers can be divided into oxidative and non--oxidative (Fig. 4).

The first group includes:

– gas-phase oxidation,

– liquid-phase oxidation (chemical [12] or electroche-mical [11]),

– catalytic oxidation.

In contrast, non-oxidative surface treatment of carbon fibers is based on the deposition of more active forms of carbon on the fibers' surface. Surface charge, hydropho-bicity and chemical reactivity can be altered by both phy-sical as well as chemical modifications. Chemical modi-fications allow for the covalent attachment of functional groups, the presence of which increases the wettability, dispersity and reactivity of the CF surface and enables its further functionalization. On the other hand, physical film deposition and/or coating, improves the mechani-cal strength and chemical stability of CFs and results in increased functionality by affecting electrical conducti-vity, or the ability to activate selectively certain regions on the fiber surface.

All the methods of surface functionalization led to an increase in adhesion between the matrix and the fibers that reinforce the composite. Considering the possible effects of modification, it can be described as follows:

– modification of carbon fibers significantly affects the roughness profile and morphology of their surface.

– increased roughness of the fibers, consequently, leads to improved bonding between the fibers and the matrix.

– surface treatment, affects not only the outer layer, but also the chemical structure of the fibers.

– the optimal choice of the CFs surface treatment is necessary, and the main factor should be the final appli-cation of the material.

Chemical surface functionalization of carbon fibers

Chemical methods of the carbon fibers modification, involve the introduction of various functional groups on the fibers surface, which increases their reactivity. CF oxi-dation results in the removal of the loosely bound, most defected carbon surface layer. This occurs with the simul-taneous chemisorption of oxygen on the terminal carbon atoms and the formation of oxygen functional groups [13]. CF oxidation reactions can be carried out using various oxidizing reagents: nitric acid (V) (HNO_3), potassium per-manganate ($KMnO_4$), hydrogen peroxide (H_2O_2). It was found that the oxidation of carbon fibers in the liquid phase occurs under milder conditions than in the gas phase. Moreover, oxidation in the liquid phase does not degrade the structure and does not destructively affect the strength properties of the fibers. The oxidation pro-cess affects the roughness of the final material [14], fiber roughness increases with the duration of the oxidation process. During the oxidation process, the formation of various oxygen groups (carboxyl and carbonyl groups) takes place on the fibers' surface, improving the reactivity of the fibers with the matrix for the composites. Changes in the morphology of the carbon fibers surface under oxi-dation are illustrated by the images shown in the Fig. 5.

The oxidation process decreases the strength of carbon fibers. This is considered to be due to fibers crystalliza-tion [3].

A comparative study of the oxidation conditions effect on the properties of carbon fibers was performed [15]. Two oxidation methods were used, the thermal process and nitric acid oxidation [16]. The thermo-oxidation process using oxygen was carried out in the temperature range of 100–600°C, while oxidation with nitric acid was con-ducted using 68% HNO_3, at a temperature of 25°C, in the variable times from 1 up to 72 hours. The authors found that the progressive oxidation process, can cause the removal of the rough layer formed during the initial oxi-dation phase. After 1 hour, the fibers modified isother-mally, at a temperature of 200°C, completely lose their rough nature, while the typical structure of carbonized fibers is retained. At the same time, for fibers modified with nitric acid, there is only a partial reduction in the roughness profile. It should be noted that both oxidation methods significantly affect the structure of carbon fibers. Removal of amorphous carbon and exfoliation of the fiber layer were observed. An increase in the temperature of the thermo-oxidation process resulted in the formation of
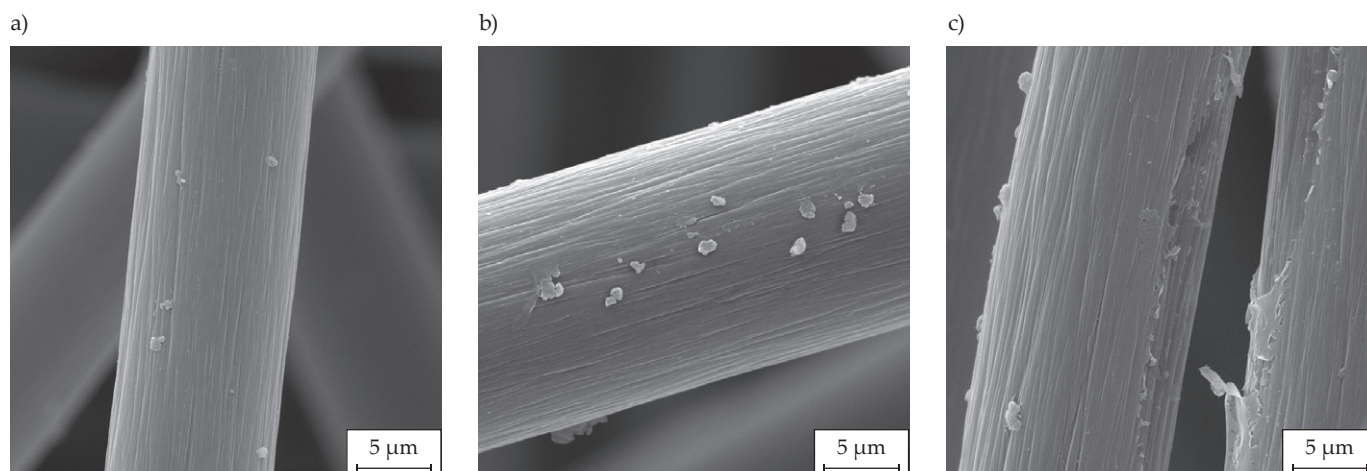
a)   b)   c)

Fig. 5. Carbon fibers surface under oxidation by HNO$_3$: a) 5 min, b) 10 min, c) 30 min

cracks and fissures < 1µm in diameter on the fiber surface, indicating the etching of graphitic structures.

Physical surface functionalization of the carbon fibers

Dip-coating method

One of the methods of physical functionalization is dip-coating. In the case of fiber-reinforced composites, this is an efficient method of modifying interfacial regions, which affects the bonding conditions of the components [16]. Dip-coating is a simple method for depositing active materials on any type of substrate, including metallic, ceramic, polymer, textile and other substrates [15]. The process involves two main steps. In the first one, coating materials are dissolved in appropriately selected solvents, while in the second, deposition on a solid substrate takes place (Fig. 6).

Depending on the handling of the process, different types of dip - coating method could be distinguished:

– sol-gel dip-coating,
– vacuum-assisted dip-coating,
– light-assisted dip-coating,
– spin-assisted dip-coating,
– multilayer dip-coating.

Fig. 6. Scheme of the dip – coating process

T a b l e 2. **Basic characteristics of dip-coating methods**

Method	Advantages	Disadvantages	Examples
Dip-coating	Simplicity of the process Ability to scale up production	Low homogeneity Relatively low degree of formation of weak bonds	Cellulose fiber coated with carbon nanotubes (CNTs) [57]
Sol-gel dip-coating	Treatment efficiency	Chemical reaction onto the fiber's surface	Thin TiO$_2$ films on cellulose fibers [58]
Spin-assisted dip-coating	Evenly deposited layer Speed of deposition	High requirements regarding equipment	Microstructure lithium-ion batteries [59]
Multilayer dip-coating	High homogeneity of the coating Multilayer structure	Relatively low efficiency	Two-stage coating of solar cell electrodes [60]
Vacuum-assisted dip-coating	Wide range of substrates to facilitate the process	High requirements regarding equipment	Cotton fabric coated with graphene oxide [61]
Light-assisted dip-coating	Wide range of coating precursors	Complex photo-chemical evaporation method	Light-assisted growth of silver nanoparticles [62]

The most important features and characteristics of each method are presented in the Table 2.

Using the immersion method, it is possible to apply multiple layers through successive immersions. As a modification of the solution dipping method, this method improves the homogeneity and/or increases the thickness of a single applied layer. Multilayer dip coating aims to achieve greater functionality of the material by applying several identical or functionally complementary layers. Layer-by-layer dip-coating is the process of alternately immersing a substrate with a defined charge in aqueous solutions of oppositely charged materials, with an intermediate rinsing process in water [17]. Compared to the standard process, the multiple method has more advantages due to the synergistic effect of the deposited layers.

Both the morphology and thickness of the coated base can be controlled by monitoring parameters such as immersion time, number of immersion cycles, substrate withdrawal speed, density, and viscosity of the coating substance.

Carbon fibers and Carbon Fiber Reinforced Composites (CFRC) are considered promising materials for medicine due to their mechanical properties and chemical structure. Carbon fiber-reinforced composite [18], which was produced based on phenolic resin with carbon fibers obtained from PAN precursor by carbonization (1000°C) and graphitization (2500°C) has been tested for its utility in medical applications [19]. The material was fragmented into millimeter-sized pieces, their surface was polished with colloidal SiO_2 and coated with a carbon-titanium layer (C: Ti) (3,3 μm) by plasma-assisted physical vapor deposition method. Both polishing and carbon-titanium coating significantly improved the biocompatibility of CFRC composites *in vitro*. Higher colonization of MG63 cells and vascular smooth muscle cells as well as lower release of carbon particles were observed. This effect was particularly enhanced with both types of surface modification.

Another example of modification is a carbon nonwoven coated with a nanohybrid coating consisting of chitosan and hydroxyapatite [20].

These materials have been used in biological studies with human bone marrow mesenchymal stem cells (hBMSCs), and the HA/CS/CFs composites were found to exhibit excellent biocompatibility. The observed biological effect is because the hybrid material has similar chemical composition, morphology, and crystallinity to natural bone minerals, indicating that it could be potentially used as a scaffold for bone tissue regeneration. An alternative to this type of functionalization is to modify the carbon fiber precursor itself by introducing active nano--additives into the fiber material [21]. Indeed, it is possible to introduce into the structure of precursor fibers, appropriately selected nano-additives, such as silica, montmorillonite or hydroxyapatite [19]. Ultimately, biocomposites with properties that allow their use in orthopedics or trauma surgery are obtained.

Solution coating as a functionalization of fibrous materials is an effective method for improving biocompatibility. This method is used not only for carbon fibers but also for the modification of a variety of polymers (with hydroxyapatite), such as ultra-high molecular weight polyethylene (UHMWPE) [22]. The immersion method has also been used to apply chitosan layers to lyocell fibers [23].

It is worth mentioning that in addition to carbon fibers, there is also increasing research into the use of nonwoven carbon fibers. Such a material, combines the properties of carbon fibers with those of nonwovens (increased specific surface area) [24, 25]. Nonwoven material also makes it easy to use other methods of physical modification, as discussed in the following sections.

PVD physical vapor deposition

Another widely used modification technique is physical vapor deposition (PVD). It is a process that allows coating a matrix with thin protective films with an anti-corrosive property. This process is already well known, so it is used in various industries [26]. PVD is a process carried out under a high vacuum, in which the coating material passes into the gas phase, followed by condensation of the vapors of the coating material, which results in the formation of a solid coating. Within this method, there are two variants: sputtering and evaporation. The undoubtedly big advantage of this process is the lack of harmful effects on the environment. Other advantages include: the formation of homogeneous coatings with an excellent adhesion, controlled morphology and the ability to create structures with gradable properties, while maintaining a wide variety and properties of coating materials [21,27]. There are known coating methods in the different systems: mono-layered, multi-layered, and multi-graduated, by using special alloy compositions. Additional advantage of the process is the possibility of changing the properties of the projecting coating throughout its whole area [28, 29, 30]. There is noticeable possibility of discontinuities or defects in the coating layer depending on the used matrix. This is largely due to the fact that sputtering and evaporation techniques are line-of-sight processes, which means that the deposited material is carried about the area from a source to the matrix [31]. Facing occurrence of the angle-of-incidence effect on the matrix surface, the coating material is mainly deposited in the areas in the direct field of the working source [32]. The result of it is the formation of various types of defects (nodal defects, holes, pores), which in the PVD process literature are referred as growth defects (to emphasize that they are the result of slow growth) [33]. Any discontinuities in the coating layer will increase the roughness of the obtained materials (Fig. 7).

Physical vapor deposition is also applicable to the carbon fibers. The reason for that is a fact of being considered as a relatively easy method of applying metallic layers that produce the intended strengthening effects,
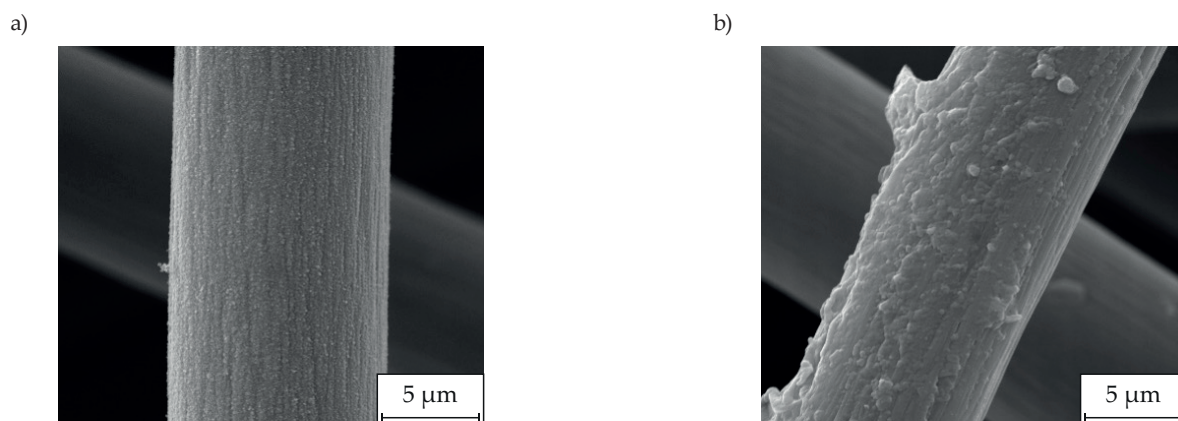
a)

b)

Fig. 7. Carbon fibers before (a) and after (b) PVD modification

such as an increase in thermal strength, an increase in electrical and thermal conductivity, or an improvement in mechanical properties. In the literature [34] there is described the use of hafnium (Hf) and hafnium-tantalum alloy (Hf-Ta) coating applied by PVD technique as protective layers in high-temperature oxidation. Coating of carbon fibers was carried out by magnetron sputtering, using various temperature conditions in the range of 25–700°C. Finally, high-temperature oxidation tests were performed on the samples after coating at a temperature of 250°C. Carbon fiber without modification was used as a control sample. The cross sections of the metallic coatings, regardless of their composition, looked similar, and continuous, adherent layers were observed, with minor defects due to temperature conditions close to the melting point of the metals used. Both coatings of hafnium and alloy of hafnium with 27% tantalum addition, were found to be thick enough to be used as CF protective coatings. In addition, the microstructure of the resulting deposit at the coating site was not altered, and therefore did not adversely affect the resistance oxidation in 1850°C.

In the different studies [35] the effect of coating carbon fibers with metallic coating (nickel and copper) on thermal and electrical conductivity as well as mechanical properties of the obtained composites, comparing to unmodified fibers were investigated. As for the choice of coating materials, nickel is described in the literature as an easy-processing metal, used primarily as the outer layer of laminates, and CFs coated with it are commercially available [36]. Copper is known for its very good thermal and electrical conductivity, and it may also provide a source of functional groups that will bind to the matrix. It also poses less of a health risk, compared to nickel [36]. Significant differences were found in the morphology of the metal-coated fibers, the nickel coating was highly homogeneous, and the metal-fiber bonding was excellent, while the copper coating was much less homogeneous, agglomerates were observed on the surface. However, the two composites obtained showed significantly improved conductivity, both in the transverse direction and along the fiber axis. The measured thermal

conductivity increased: twice for Ni and six times for Cu, compared to the uncoated fiber (along the fiber axis), and by 45 and 380%, respectively, for the same elements in the transverse direction.

PVD technique has also been tested as a physical modification of carbon fiber-reinforced polyether ether ketone (PEEK) implants [37]. It was expected that the titanium layer deposited on the surface of this type of implant would have a positive effect on the integration of the implant with bone, which would increase the range of such biomaterial's applicability. The CF/PEEK composite has adequate mechanical properties for use as load-bearing orthopedic implants (*e.g.*, screws), and has many advantages over metallic implants. However, an important limitation to the applicability of such a composite is its highly hydrophobic surface, which promotes tissue fibrosis around the implant. The implant, fabricated using the PVD technique, was characterized and inserted into the tibia of a sheep. Initial evaluation of the titanium layer indicated that it was smooth and homogeneous. However, in histological sections, delamination of the titanium coating was observed in the bone near the implant (which may indicate delamination during screw insertion). The reason for this is probably the low bond strength of the metallic coating to the substrate. Nevertheless, a marked increase in the percentage area of contact with bone was observed, compared to an implant without titanium coating.

ALD – Atomic layer deposition

Another technique of physical modification is Atomic Layer Deposition (ALD). It represents a solution particularly relevant to nanotechnology because of the control of the applied layer thickness. The technique originated from research conducted in the 1960s [38] and was originally called as Atomic Layer Epitaxy (ALE). The technique was developed in the 1970s [39], and 20 years later, it acquired its current name [40, 41]. The operating principle of ALD is the successive cycles of surface reactions between the molecules of the vapor-phase applied film (precursor) and the matrix (substrate). In between these

cycles, purification steps are carried out. The application of successive layers is a self-limiting process [42], and the purification cycles that follow, involve the removal of unreacted precursor molecules and other volatile reaction byproducts [43]. The following two stages are factors in determining the thickness of the deposited film [44,45]. The growth rate of the applied layer is defined as growth per cycle (GPC), and the thickness of applied layer could be precisely controlled on atomic level by the change of the number of the ALD process cycles. ALD technique is considered as a modification of Chemical Vapor Deposition (CVD) [46]. Common feature for both is the use of volatile precursors and the removal of gaseous reaction by-products through the flow of an inert gas stream. However, it is worth stressing out that the advantage of ALD over CVD is its 'self-limiting character'. The CVD reaction is heterogeneous and most often leads to coatings with inhomogeneous thickness or unshaped layer growth, depending on the substrate [47]. The ALD reaction is stopped when all available reactive sites on the substrate surface have been utilized. Important for obtaining the intended films is to keep the process temperature within a certain range [42]. Typical ALD process can be carried out regardless of the type of substrates, which are selected for the specific application of the final product. Substrates of diverse origins and geometries are used, such as one-dimensional (1D) structures: nanowires, carbon nanotubes, graphene structures and organic materials, nitrides, oxides, halides, and metals. The ALD method has found applications in many fields, such as solar energy conversion (core-shell nanowire lamination) [48], Synthesis of the components of lithium-ion batteries [48], fabrication of complementary metal-oxide semiconductors [49], field-effect transistors [50], or fabrication of semiconductor devices.

Despite the current wide range of applications, the ALD technique is not without limitations. These include, for example, the cost of metal precursors, such as platinum [51], or the high toxicity of the used compounds [52]. In addition, coating at reduced temperatures is a major challenge, due to insufficient activity of the precursor against temperature-sensitive substrates [52].

Like PVD, the ALD technique has also been used to create coatings on carbon fibers to increase resistance to high-temperature oxidation treatment, improve the mechanical properties of the composite, or increase its bioactivity. Roy et al. [53] have used this method for the formation of aluminum coatings on carbon fibers, with the aim of increasing CF resistance to oxidation at higher temperatures. They proved that there is a correlation between the thickness of the applied layer and the temperature resistance. Under optimal conditions, the aluminum-coated carbon fibers oxidized only at 660°C, which is twice higher compared to the result for unmodified fibers. The same research team [54] used coatings containing aluminum and titanium deposited on CF. Different variants of the applied coatings were tested, containing single metals, their combinations and the formation of double layers. The highest resistance to oxidation treatment (750°C) showed carbon fibers initially coated with a layer of titanium (20 nm), and then aluminum (30 nm).

Another research [55] has shown that carbon fiber-based materials modified with ZnO nanolayer can be used to develop new composites with enhanced mechanical properties. A titanium oxide layer deposited by the ALD technique on carbon fiber also proved to be an effective adsorbent of organic dyes [55]. It has been proven that such a coating exhibits extremely high absorption of methylene blue (MB) under darkroom conditions. Moreover, it has been shown that the adsorption capacity of the obtained coatings can be regenerated by irradiation and photocatalytic degradation of the adsorbed MB.

ALD has also proven to be a useful modification technique in terms of coating the carbon fibers for highly specialized applications. The ALD method has been used [56] to produce CF-based nanomaterials reinforced and coated with a metallic (CuAl) layer. In the first phase, carbon fibers were coated with a thin uniform layer of Al_2O_3, which was then hydrothermally treated to obtain the actual material. The resulting nanomaterials were used to develop a simple and sensitive biosensor for the calorimetric determination of glucose.

CONCLUSIONS

Carbon fibers have many unique characteristics (very good mechanical and electrical properties, stiffness, chemical inertness) that predestine them for applications in many fields. Nevertheless, limitations due to their hydrophobic properties, make carbon fibers the object of various modifications. Modification of carbon fibers significantly affects the morphology and roughness of their surface, which consequently improves the adhesion parameter of this type of reinforcement to the composite matrix.

Methods for functionalizing carbon fibers include oxidative and non-oxidative processes. Chemical and physical methods are also used to modify CF. Among chemical methods, oxidation reactions are the most used, while between physical methods, the dip - coating method is gaining interest.

The dip-coating method can be implemented in different ways: solution coating, vacuum-assisted coating, or multilayer coating. For carbon fibers, the multilayer method is the most effective, which is due to the synergistic effect of all the layers applied.

Coating carbon fibers with biologically active agents leads to obtaining the composite materials with enhanced biocompatibility.

REFERENCES

[1] Chung D.D.L.: "Carbon Fiber Composites", Elsevier Inc., Butterworth-Heinemann 2012, p. 81.
https://doi.org/10.1016/C2009-0-26078-8

[2] Kobets L.P., Deev I.S.: *Composite Science and Technology* **1998**, *57*, 1571.
https://doi.org/10.1016/S0266-3538(97)00088-2

[3] Mayer P., Kaczmar J.W.: *Tworzywa Sztuczne i Chemia* **2008**, *6*, 52.

[4] Noisternig J.F.: *Applied Composite Materials* **2000**, *7*, 139.
https://doi.org/10.1023/a:1008946132034

[5] Wambua P., Ivens J., Verpoest I.: *Composite Science and Technology* **2003**, *63*, 1259.
https://doi.org/10.1016/S0266-3538(03)00096-4

[6] https://materialyinzynierskie.pl/kompozyty-zbrojone-wloknem-weglowym-cfrp/ (access date 18.03.2023).

[7] Królikowski W.: „Tworzywa wzmocnione i włókna wzmacniające", Wydawnictwa Naukowo-Techniczne 1988.

[8] van der Woude L.H.V., de Groot S., Janssen T.W.J.: *Medical Engineering and Physic* **2006**, *28*, 905.
https://doi.org/10.1016/j.medengphy.2005.12.001

[9] Chand S.: *Journal of Materials Science* **2000**, *35*, 1303.

[10] Weitzsacker C.L., Xie M., Drzal L.T.: *Surface and Interface Analysis* **1997**, *27*, 233.
https://doi.org/10.1002/(SICI)1096-9918(199702)25:2<53::AID-SIA222>3.0.CO;2-E

[11] Delamar M., Desarmot G., Fagebaume O., Hitmi R. *et al.*: *Carbon* **1997**, *35*, 801.
https://doi.org/10.1016/S0008-6223(97)00010-9

[12] Ibarra L., Macias A., Palma E.: *Journal of Applied Polymer Science* **1996**, *61*, 2447.
https://doi.org/10.1002/(SICI)1097-4628(19960926)61:13<2447::AID-APP24>3.0.CO;2-#

[13] Chukov D.I., Stepashkin A.A., Gorshenkov M.V. *et al.*: *Journal of Alloys Compounds* **2014**, *586*, 5459.
https://doi.org/10.1016/j.jallcom.2012.11.048

[14] Tiwari S., Bijwe J., Panier S.: *Wear* **2011**, *271*, 2252.
https://doi.org/10.1016/j.wear.2010.11.052

[15] Kar K.K.: "Handbook of Nanocomposite Supercapacitor Materials III. Selection", Springer International Publishing 2021.

[16] Tang X., Yan X.: *Journal of Sol-Gel Science and Technology* **2017**, *81*, 378
https://doi.org/10.1007/s10971-016-4197-7.

[17] Li Y., Wang X., Sun J.: *Chemical Society Reviews Journal* **2012**, *41*, 5998.
https://doi.org/10.1039/c2cs35107b

[18] Bacáková L., Starý V., Kofronová O.: *Journal of Biomedical Materials Research* **2001**, *54*, 567.

[19] Rajzer I., Menaszek E., Bacakova L. *et al.*: *Fibres and Textiles of Eastern Europe* **2013**, *99*, 102.

[20] Liu Y. T., Long T., Tang S. *et al.*: *Materials Letters* **2014**, *128*, 31.
https://doi.org/10.1016/j.matlet.2014.04.117

[21] Kim M., Kim S., Kim T. *et al.*: *Coatings*, **2017**, *7*, 231.
https://doi.org/10.3390/coatings7120231

[22] Navarro C.H., Moreno K.J., Chavez-Valdez A. *et al.*: *Wear* **2012**, *282*, 76.
https://doi.org/10.1016/j.wear.2012.02.004

[23] Janjic S., Kostic M., Vucinic V. *et al.*: *Carbohydrate Polymers* **2009**, *78*, 240.
https://doi.org/10.1016/j.carbpol.2009.03.033

[24] Fraczek-Szczypta A., Rabiej S., Szparaga G. *et al.*: *Materials Science Engineering C* **2015**, *51*, 336.
https://doi.org/10.1016/j.msec.2015.03.021

[25] Frączyk J., Magdziarz S., Stodolak-Zych E. *et al.*: *Materials* **2021**, *14*, 3198.
https://doi.org/10.3390/ma14123198

[26] Prengel H.G., Pfouts W.R., Santhanam A.T.: *Surface and Coatings Technology* **1998**, *102*, 183.
https://doi.org/10.1016/S0257-8972(96)03061-7

[27] Silva F., Martinho R., Andrade M. *et al.*: *Coatings* **2017**, *7*, 28.
https://doi.org/10.3390/coatings7020028

[28] Skordaris G., Bouzakis K.D., Kotsanis T. *et al.*: *Surface and Coatings Technology* **2016**, *307*, 452.
https://doi.org/10.1016/j.surfcoat.2016.09.026

[29] Abdullah M. Z., Ahmad M.A., Abdullah A.N. *et al.*: *Procedia Engineering* **2016**, *148*, 254.
https://doi.org/10.1016/j.proeng.2016.06.612

[30] Imbeni V., Martini C., Lanzoni E. *et al.*: *Wear* **2001**, *251*, 997.
https://doi.org/10.1016/S0043-1648(01)00706-2

[31] Panjan P., Drnovšek A., Gselman P. *et al.*: *Coatings* **2020**, *10*, 447.
https://doi.org/10.3390/coatings10050447

[32] Rao D.S., Valleti K., Joshi S.V. *et al.*: *Journal of Vacuum Science and Technology A* **2011**, *29*, 031501.
https://doi.org/10.1116/1.3563600

[33] Panjan P., Cekada M., Panjan M. *et al.*: *Vacuum* **2012**, *86*, 794.
https://doi.org/10.1016/j.vacuum.2011.07.013

[34] Andréani A.S., Poulon-Quintin A., Rebillat F.: *Surface and Coatings Technology* **2010**, *205*, 1262.

[35] Bard S., Schönl F., Demleitner M. *et al.*: *Polymers* **2019**, *11*, 823.
https://doi.org/10.3390/polym11050823

[36] Yu S., Park B.I., Park C. *et al.*: *ACS Applied Materials Interfaces* **2014**, *6*, 7498.
https://doi.org/10.1021/am500871b

[37] Devine D.M., Hachn J., Richards R.G. *et al.*: *Journal of Biomedical Materials Results - Part B Applied Biomaterials* **2013**, *101*, 591.

[38] Ahvenniemi E. Akbashew A.R., Ali S. *et al.*: *Journal of Vacuum Science and Technology A* **2017**, *35*, 010801.
https://doi.org/10.1116/1.4971389

[39] *Pat.US* 4 058 430 (1977).

[40] Knez M., Nielsch K., Niinistö L.: *Advanced Materials* **2007**, *19*, 3425.
https://doi.org/10.1002/adma.200700079

[41] Miikkulainen V., Leskelä M., Ritala M. *et al.*: *Journal of Applied Physics* **2013**, *113*, 021301.

https://doi.org/10.1063/1.4757907

[42] George S.M.: *Chemical Review* **2010**, *110*, 111.
https://doi.org/10.1021/cr900056b

[43] Mohseni H., Scharf T.W.: *Journal of Vacuum Science and Technology A* **2012**, *30*, 01A149.

[44] Miikkulainen V., Leskelä M., Ritala M.: *Journal of Applied Physics* **2013**, *113*.

[45] Puurunen R.L.: *Journal of Applied Physics,* **2005,** *97*.

[46] Malandrino G.: "Chemical vapour deposition: precursors, processes and applications", Angewandte Chemie International Edition 2009, p. 7478.

[47] Parsons G.N., George S.M.,Knez M.: *MRS Bulletin* **2011**, *36*, 865.
https://doi.org/10.1557/mrs.2011.238

[48] Meng X., Yang X.Q., Sun X.: *Advanced Materials* **2012**, *24*, 3589.
https://doi.org/10.1002/adma.201200397

[49] Lim J. Y., Pezeshki A., Oh S. *et al.: Advanced Materials* **2017**, *29*, 1701798.
https://doi.org/10.1002/adma.201701798

[50] Wang X., Zhang T.B., Yang W. *et al.: Applied Physics Letters* **2017**, *110,* 053110.
https://doi.org/10.1063/1.4975627

[51] Wen L., Mi Y., Wang C. *et al.: Small* **2014**, *10*, 3162.
https://doi.org/10.1002/smll.201400436

[52] Choi K.H., Ali K., Kim C.Y. *et al.: Chemical Vapour Deposition* **2014**, *20*, 118.
https://doi.org/10.1002/cvde.201307082

[53] Roy A.K., Baumann W., Schulze S. *et al.: Journal of the American Ceramic Society* **2011**, *94*, 2014.

https://doi.org/10.1111/j.1551-2916.2010.04340.x

[54] Roy A. K., Schulze S., Hietschold M. *et al.: Carbon* **2012**, *50*, 761.
https://doi.org/10.1016/j.carbon.2011.09.023

[55] Dey N.K., Kim M.J., Kim K.D. *et al.: Journal of Molecular Catalysis A Chemica,* **2011**, *337*, 33.
https://doi.org/10.1016/j.molcata.2011.01.010

[56] Wu L., Wan G., Shi S. *et al.: New Journal of Chemistry* **2019**, *43*, 5826.
https://doi.org/10.1039/c8nj06217j

[57] Qi H., Liu J., Deng Y. *et al.: Journal of Materials Chemistry A* **2014**, *2*, 5541.
https://doi.org/10.1039/c3ta14820c

[58] Foruzanmehr Mr., Vuillaume P.Y., Robert M. *et al.: Materials Design* **2015**, *85*, 671.
https://doi.org/10.1016/j.matdes.2015.06.105

[59] Roberts M., Huang A.F., Johns P. *et al.: Journal of Power Sources* **2013**, *224*, 250.
https://doi.org/10.1016/j.jpowsour.2012.09.103

[60] Pu D., Zhou W., Chen J. *et al.: RSC Advances* **2015**, *5*, 100725.
https://doi.org/10.1039/c5ra20097k

[61] Tang X., Tian M., Qu L. *et al.: Synthetic Metals* **2015**, *202*, 82.
https://doi.org/10.1016/j.synthmet.2015.01.017

[62] Kafizas A., Parry S.A., Chadwick A.V. *et al.: Physical Chemistry Chemical Physics* **2013**, *15*, 8254.
https://doi.org/10.1039/c3cp44513e

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