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Polyaniline and its composites with carbon nanomaterials: preparation, properties, application

© Irina V. Gutnik[a]✉, Tatyana P. Dyachkova[a], Elena A. Burakova[a],
Evgeniy N. Tugolukov[a], Artem V. Rukhov[a], Georgiy A. Titov[a]

[a] *Tambov State Technical University, Bld. 2, 106/5, Sovetskaya St., Tambov, 392000, Russian Federation*

✉ i.v.gutnik@yandex.ru

Abstract: The increased attention of researchers to electrically conductive polymers, including polyaniline (PANI), is due to the wide possibilities of its use in the production of supercapacitors, energy storage devices, anticorrosive coatings, detectors, sensors, solar cells, antimicrobial materials, sorbents, and coatings that absorb electromagnetic radiation. However, the instability of the PANI properties during operation limits the practical use of the polymer. In this regard, to date, many attempts have been made to stabilize the characteristics and increase the service life of polyaniline. Thus, new composite materials, which combine PANI and one or more other components, including carbon nanomaterials (carbon nanotubes, graphene, graphene oxide, reduced graphene oxide, mesoporous carbon), montmorillonite, metals, chalcogenides, conductive polymers,were developed. The purpose of this study is to summarize the information accumulated to date on electrically conductive polyaniline and its composites with carbon nanomaterials (CNM), as well as to demonstrate their potential and future prospects. The paper describes the structure and properties of the polymer. Chemical and electrochemical approaches to the synthesis of PANI and composites based on it are considered, attention is paid to the influence of synthesis conditions on the structure and properties of the final reaction products. A brief description of the application of polyaniline and its composites with CNM is given.

Keywords: polyaniline; carbon nanotubes; functionalized carbon nanotubes; graphene; composite.

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Полианилин и его композиты с углеродными наноматериалами: получение, свойства, применение

© И. В. Гутник[a]✉, Т. П. Дьячкова[a], Е. А. Буракова[a],
Е. Н. Туголуков[a], А. В. Рухов[a], Г. А. Титов[a]

[a] *Тамбовский государственный технический университет,*
ул. Советская, 106/5, пом. 2, Тамбов, 392000, Российская Федерация

✉ i.v.gutnik@yandex.ru

Аннотация: Повышенное внимание исследователей к электропроводящим полимерам, в том числе к полианилину (ПАНИ), обусловлено широкими возможностями его применения при производстве суперконденсаторов, накопителей энергии, антикоррозионных покрытий, датчиков, сенсоров, элементов солнечных батарей, антимикробных материалов, сорбентов, покрытий, поглощающих электромагнитное излучение. Однако нестабильность свойств ПАНИ в ходе эксплуатации ограничивает практическое применение полимера. В связи с этим к настоящему времени предпринято множество попыток, позволяющих стабилизировать характеристики и увеличить срок службы полианилина. Например, разработаны новые композиционные материалы, сочетающие в себе ПАНИ и один или несколько других компонентов, среди которых углеродные наноматериалы (углеродные нанотрубки, графен, оксид графена, восстановленный оксид графена, мезопористый углерод), монтмориллонит, металлы, халькогениды, проводящие полимеры. Цель исследования – обобщить сведения, накопленные к настоящему времени об электропроводящем полианилине и его композитах с углеродными наноматериалами (УНМ), продемонстрировать их потенциал и будущие перспективы. Даны описания строения и свойств полимера.

Рассмотрены химические и электрохимические подходы к синтезу ПАНИ и композитов на его основе, уделено внимание влиянию условий синтеза на структуру и свойства конечных продуктов реакции. Дана краткая характеристика областей применения полианилина и его композитов с УНМ.

Ключевые слова: полианилин; углеродные нанотрубки; функционализированные углеродные нанотрубки; графен; композит.

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1. Introduction

Since the discovery of polyaniline (PANI), which belongs to the class of electrically conductive polymers, to the present time there has been an increase in the number of studies related to this material. This is primarily due to the unique properties of PANI [1]. PANI belongs to the class of conjugated polymers, so it can have conductivity close to metallic. PANI is also distinguished by ease of synthesis and doping with protic acids, environmental stability and low cost [2–4]. However, changes in electrical conductivity during operation, low cyclic stability, mechanical degradation, and processing complexity significantly limit the practical use of the polymer [5, 6]. It is known that charge/discharge processes are accompanied by swelling, shrinkage and destruction of the polymer during doping/dedoping processes, which leads to a decrease in cycle stability. In addition, PANI degradation can occur at relatively high potentials. The consequence of this is the low operating potential of PANI electrodes.

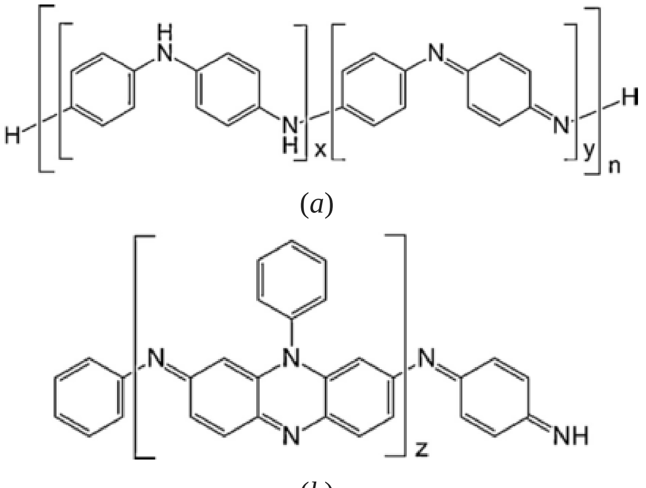
To eliminate the above defects, researchers usually combine polyaniline with other materials (carbon nanotubes (CNTs), graphene (G), graphene oxide (GO), cellulose, montmorillonite, metal oxides). As a result, new materials are obtained, which are characterized by increased capacitive characteristics and high chemical stability [7]. For example, a PANI composite with carbon nanotubes, synthesized for use as an electrode material for a supercapacitor, demonstrates a fairly high specific capacitance of 1266 $F \cdot g^{-1}$, exceeding the capacitance of the original components [8]. It has also been shown that PANI/CNT hybrids exhibit a synergistic effect [9].

On the one hand, the carbon dispersed carrier increases the accessible surface of PANI, on the other hand, it creates an electrically conductive frame, which makes it possible, by increasing electronic and ionic conductivity, to increase the electrical power removed from the electrode. Also, this framework is more rigid than PANI itself, which makes it possible to stabilize the porous structure of the polymer with multiple repetition of charge/discharge.

The possibility of stabilizing the PANI properties by synthesizing composites based on it gives rise to a large number of studies on this topic, the results of which are reflected in both scientific and review articles. However, in the latter, there is mainly a generalization of the results obtained within specific areas of practical application of composites (for example, in supercapacitors, sorbents). With this approach, the effectiveness of the synthesized composites is demonstrated in only one area of application. There is also no systematic information on the dependence of the characteristics of composites on their composition. In this regard, this review summarizes the results accumulated to date in the field of preparation and characterization of PANI composites with carbon nanomaterials. Attention is paid to the influence of the mass composition of composites on their morphological and operational characteristics. A brief description of promising areas of application of these composites is presented. The review also provides information on the structure, properties and methods of producing PANI, which can be used by researchers to select optimal conditions for the synthesis of composites with given parameters.

2. Chemical structure and properties of PANI

PANI has the longest history of research among electrically conductive polymers. This polymer was discovered in the middle of the 19th century [10]. It was then known as “aniline black” (a term in those days used for any product obtained by the oxidation of aniline). The discovery of PANI can probably be considered the experiments of Runge [11]. Later, Fritsche and Leteby continued to study the oxidation process of aniline and discovered a change in the color of the resulting precipitate [12–14]. The results obtained by scientists in the century before last served as a prerequisite for studying the process of obtaining “black aniline”, as well as for studying its redox and acid-base transformations.



(*a*)

(*b*)

Fig. 1. Molecular structure of various redox forms of linear aniline octamers, proposed at the beginning of the 20th century (*a*: $x + y = 4$, $n = 1$; leucoemeraldine: $x = 4$, $y = 0$; protoemeraldine: $x = 3$, $y = 1$; emeraldine: $x = 2$, $y = 2$; nigranilin: $x = 1$, $y = 3$; pernigraniline: $x = 0$, $y = 4$) and black aniline (*b*: $z = 3$) [15]

The terms emeraldine and nigraniline were coined for the various oxidized/reduced forms of aniline black. At the beginning of the 20th century, the concepts "leucoemeraldine", "protoemeraldine" and "pernigraniline" were introduced to designate linear combinations of aniline octamers with varying degrees of oxidation, i.e. with different numbers of N-phenyl-benzoquinonediimine and 4-aminodiphenylamine fragments in the main chain (Fig. 1*a*) [15].

The molecular weight of PANI in the form of emeraldine is significantly higher than that of octamers, indicating the existence of intermediate oxidation states between leucoemeraldine and emeraldine ($x > y$, $y \geq 1$, Fig. 1*a*), which could be designated as protoemeraldine, corresponding to $x / y \sim 3$, as well as between emeraldine and pernigraniline ($x < y$, $x \geq 1$, Fig. 1*a*), which can be designated as nigraniline, as in the case of $x / y \sim 1/3$ [16].

In 1965, information that emeraldine has high conductivity appeared [17]. At the end of the last century, scientists discovered the possibility of transitioning from one form of PANI to another. For example, emeraldine can be converted from a base to a salt. This process is accompanied by a color change from blue to green (Fig. 2). Based on the results of these studies, a paper was published where it was reported that the transition of emeraldine to this state is accompanied by a sharp increase in conductivity by more than 10 orders of magnitude – up to 1–5 $S \cdot cm^{-1}$ [18].

Multiple studies conducted over the past decades allow us to conclude that the emeraldine salt of PANI (PANI-ES) contains localized/delocalized radical cations (polarons) and dications (bipolarons) in different proportions. Their content depends on the synthesis conditions and isolation procedures [19] (Fig. 2).

The transition of PANI in the form of emeraldine base (PANI-EB) to PANI-ES is carried out using doping, which can be done in two ways: oxidation (p-doping, when the doping component accepts electrons) or reduction (n-doping - the doping component gives up electrons) neutral polymer with a modifying additive [4].

Proton donors, usually acids (hydrochloric, sulfuric, sulfonic acids, etc.) are used to dope PANI. The electrical conductivity of doped PANI can be influenced by a number of factors, including the oxidation state of the polymer, the type of protic acid, the degree of protonation, the moisture content of the polymer, and the morphology of the polymer chain [20].

3. Methods for obtaining PANI

Currently, there are several methods for obtaining PANI. The most common one is the oxidative polymerization of aniline. There are chemical [21–24], electrochemical [25], and enzymatic [26] polymerization.

During chemical synthesis in an acidic environment, the aniline monomer or salt (aniline hydrochloride or sulfate) is converted into a conjugated polymer. Distinctive features of this method are the high yield of the target reaction product (about 90–95 % of the theoretically calculated one), as well as the relatively high electrical conductivity (1–5 $S \cdot cm^{-1}$) of the synthesized material [4].

To date, significant experimental material has been accumulated on the relationship between the properties of PANI obtained by chemical polymerization and synthesis conditions. Among the synthesis parameters that most significantly influence the properties of the final product are the nature of the oxidizing agent, pH, concentration of reagents, and polymerization temperature [27, 28].

It is known that PANI can have different morphologies (nanofibers, nanorods, nanotubes, nanospheres, granules). It has been proven that it depends on the nature of the oxidizing agent or the presence of additives in the reaction mixture [29]. For example, by varying the synthesis conditions, it is possible to obtain PANI with a granular structure [30], and in a weakly acidic environment, PANI is obtained in the form of nanotubular particles [31].

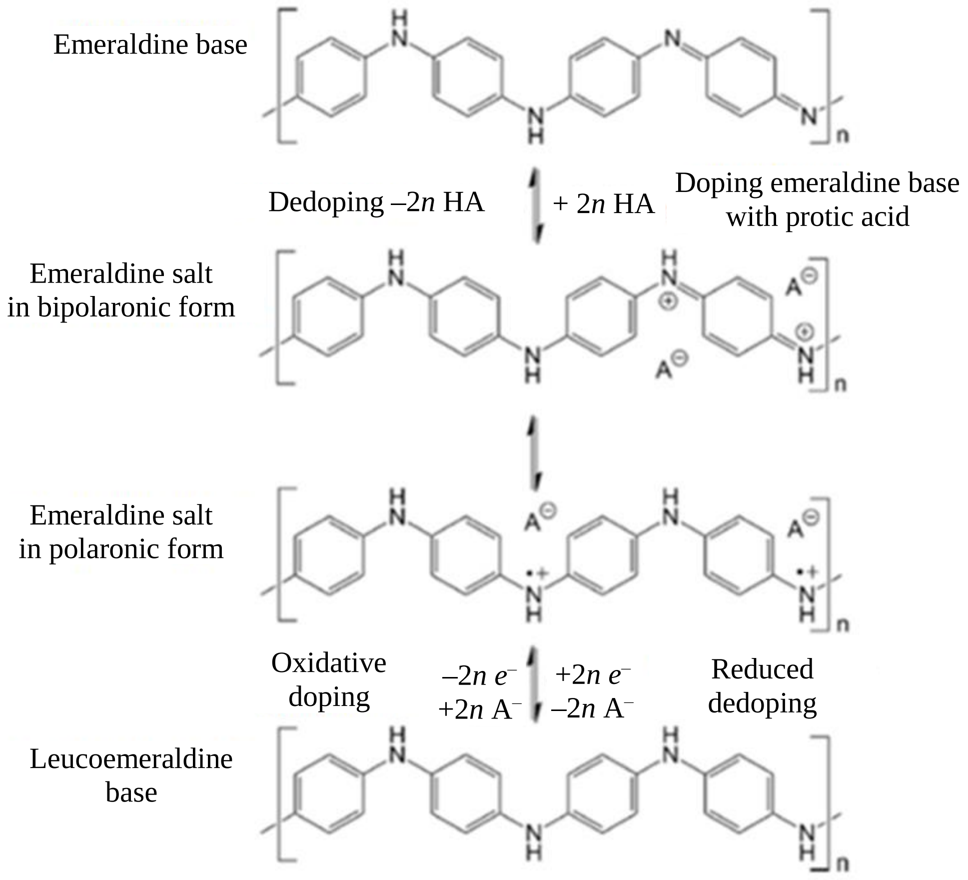


Fig. 2. Oxidative doping of leucoemeraldine base and doping emeraldine base with protic acid; A is anion

Various PANI structures are characterized by a set of morphological features (shape of structural units, specific surface area, pore size), which determine the accessibility of PANI macromolecules to electrolyte ions, and the electronic and redox properties determine the maximum possible power and energy intensity of devices based on it [32–34].

The main methods for carrying out electrochemical synthesis are galvanostatic (at a constant current) [35–37], potentiostatic (at a constant electrochemical potential) [38] and potential cycling modes [39]. The yield, morphology, electrochemical behavior, adhesion to the electrode, optical properties and other characteristics of the PANI film obtained by electrosynthesis are determined by polymerization conditions, such as the type and concentration of the electrolyte, the nature of the electrode, and synthesis modes [35].

Most often, the electrochemical synthesis of PANI is based on the anodic oxidation of aniline at various electrodes. This is due to the possibility of obtaining a purer polymer without oxidizing agent impurities, as well as the possibility of controlling the thickness of the film and observing the process of its formation using various physical and chemical methods (optical, electrochemical, etc.). Moreover, the molecular weight of PANI synthesized by electrochemical polymerization methods is usually lower than that of chemical synthesis [40].

Compared to chemical polymerization, electrochemical synthesis is faster and does not require the use of oxidizing agents and additives. The advantages of the method also include the ability to regulate the conditions (potential and current) of PANI deposition and the almost complete absence of by-products. At the same time, the morphological forms of PANI are not so diverse: nanofibers, nanogranules, or thin films on the surface of the substrate [41–43].

However, the electrochemical method is only suitable for producing polymer in small quantities, while the chemical method allows the production of polymer in large volumes [44].

The processes of converting aniline into PANI during chemical and electrochemical polymerization are similar to each other and occur in several stages (Table 1) [30].

As findings show, the duration of the induction period depends on the synthesis conditions and can increase with a decrease in the initial temperature of aniline oxidation or shorten with increasing acid concentrations [45].

Table 1. Characteristics of the stages of aniline oxidative polymerization

Stage	Observed phenomena	Products formed
Rapid exothermic oxidation of neutral aniline molecules	Increase in temperature, decrease in pH	Non-conducting oligomers
Induction period	Temperature remains virtually unchanged, pH decreases moderately	Aniline trimers
Rapid polymerization of anilinium cations	Rapid heat release is accompanied by the formation of protons	Oligomeric and polymeric products

The induction period also becomes shorter when the reacting mixture contains an inert solid material with a high surface area (carbon nanotubes, graphite) [46]. This is explained by the phenomenon of adsorption of oligomers and the formation of nucleates on such substrates.

The decrease in pH during oxidative polymerization is explained as follows: during the formation of bonds between aniline molecules and oligomers or polymers, hydrogen atoms are eliminated in the form of protons and form sulfuric acid with the persulfate reduction product [47–51].

The course of the reaction and the nature of the final product (structure, physicochemical properties, redox form) are influenced by factors such as the acidity of the medium, the nature and concentration of the oxidizing agent.

Aniline oxidation can be started in an acidic or alkaline environment. In this case, some phases may be absent depending on the initial pH of the reacting mixture. If oxidation begins in an alkaline environment, oligomers quickly form and the reaction mass becomes brown.

Conductive forms of PANI are formed in an acidic environment. In this case, practically no exothermic formation of brown oligomers is observed. A low concentration of neutral aniline molecules slows down the formation of short oligomers (mainly semidine dimers). The light blue color visible at this stage is due to the formation of an oxidized dimer. Semidines subsequently participate in the formation of trimers (nucleates), which become initiation centers for the growth of PANI chains. As a result, the polymer is the main product of the reaction; oligomers are present only in minor quantities [52].

The nature of the oxidizing agent, especially its redox potential, has a significant impact on the morphology and properties of PANI [53]. Persulfates (ammonium persulfate and potassium persulfate [54–58] and iron chloride $FeCl_3$ [59–62] are most often used as oxidizing agents in the synthesis of PANI. However, when using $FeCl_3$, polymerization proceeds at a lower rate, since its redox potential (0.77 V) is lower than that of ammonium persulfate (2.0 V) [63]. However, ammonium persulfate also has disadvantages: it is stoichiometrically consumed in the reaction, which leads to the formation of acidic by-products during the synthesis of the polymer [64]. For environmentally friendly synthesis of PANI, the use of $FeCl_3$ and ozone as a catalyst and oxidizer, respectively, has been proposed [65]. The only byproduct formed during the reaction under these conditions is water.

When ammonium persulfate is used as an oxidizing agent, the molar ratio “aniline: ammonium persulfate” (r) has a different effect on the yield, elemental composition, electrical conductivity and degree of oxidation of the resulting product. At $r \leq 1.15$, the characteristics of PANI are practically independent of the molar ratio. At $r > 1.15$, overoxidation of PANI accompanied by a decrease in the yield of the polymer, its conductivity, and a noticeable change in its morphology [66] is observed. The optimal molar ratio “aniline: ammonium persulfate” is 1 : 1.25 [4]. An increase in the concentration of ammonium persulfate by two times compared to the concentration of aniline leads to the rupture of polymolecular chains, the formation of quinoid compounds and overoxidized forms of PANI. The use of ammonium persulfate in an amount less than half that of aniline causes a decrease in the yield of PANI to 40–50 %. A number of authors believe [22, 67] that ammonium persulfate is involved in the processes of both initiation and growth of chains.

A number of other compounds are also used as oxidizing agents: manganese oxides [68–70], potassium (VI) dichromate $K_2Cr_2O_7$ [71], cerium (IV) sulfate $Ce(SO_4)_2$ [72], copper (II) chloride $CuCl_2$ [73], copper (II) nitrate $Cu(NO_3)_2$ [74], potassium ferricyanide ($K_3(Fe(CN)_6)$ [75] and sodium vanadate ($NaVO_3$) [76]. Compounds of noble metals (Au (II), Pt (IV), Pd (II), Ag (I)) [77], hydrogen peroxide [78, 79], potassium permanganate [80, 81] are also used as oxidizing agents.

In the case of using oxidizing agents such as cerium (IV) sulfate and potassium dichromate at higher concentrations ($r > 1.15$), a complexation reaction probably occurs, which leads to the production of products containing a large percentage of the metal [66].

There is information about the use of a mixture of oxidizing agents, including $FeCl_3$ / H_2O_2 [82] and KIO_3 / NaClO [83]. To accelerate the synthesis of PANI, researchers resorted to the use of catalysts, which are enzymes, for example, horseradish peroxidase [84], enzymes of the oxidoreductase class [85].

A number of researchers propose unconventional methods for the synthesis of PANI: polymerization of aniline under the influence of X-ray irradiation in the presence of nitrate ions [86]; dispersion polymerization in a weak magnetic field [87]; matrix synthesis of PANI on a solid support [88]; oxidation of aniline hydrochloride with ammonium persulfate in non-aqueous media (acetone, methanol, toluene) [89]; plasma polymerization of aniline [90], photoinduced polymerization [91].

4. Preparation and properties of PANI composites with carbon nanomaterials

4.1. PANI / CNT composites

Currently, to obtain nanocomposites of PANI with carbon nanotubes, the method of oxidative polymerization of aniline on the surface of CNTs is most often used [93–99]. This is due to the fact that this approach has a number of advantages over other methods. Thus, the ability to change synthesis conditions opens up prospects for obtaining materials with specified characteristics (specific capacitance, electrical conductivity, specific surface area) for a specific field of practical application. It is also possible to implement this method on an industrial scale [92].

Studies of the morphological features of composites have shown that in composites a layer of polymer, the thickness and roughness of which is determined by the mass fraction of each component, uniformly covers the surface of the CNT [100]. It is noted that, in comparison with emeraldine, PANI deposited on the surface of CNTs has an increased content of quinonediimine fragments. This is explained by stacking interactions between PANI and carbon nanotubes [93].

There is information about the influence of the composition of composites on their characteristics. It has been shown that PANI/CNT composites have higher electrical conductivity compared to the value of this parameter for individual components (PANI and carbon nanotubes) [49]. It has been experimentally shown that the initial PANI has the lowest electrical conductivity; with increasing CNT content in the composite, an increase in electrical conductivity is observed (Table 2). It is assumed that the increase in electrical conductivity is due to the presence of interaction between the amino groups of PANI and CNTs, which facilitates charge transfer between the polymer and carbon nanotubes [100].

Table 2. Electrical conductivity of PANI and its composites with carbon nanotubes, characterized by different mass contents of CNTs

Composite	Electrical conductivity, $S \cdot cm^{-1}$	Source
PANI/CNT (0.2 wt. %)	$0.8 \cdot 10^{-3}$	[100]
PANI/CNT (10 wt. %)	$6.6 \cdot 10^{-2}$	
PANI	$1.0 \cdot 10^{-2}$	[101]
PANI/MWCNT (0.5 wt. %)	$2.9 \cdot 10^{-1}$	
PANI/MWCNT (1 wt. %)	1.10	
PANI	0.18	[102]
PANI/MWCNT (5 wt. %)	0.85	
PANI/MWCNT (15 wt. %)	1.10	
PANI	0.17	[103]
PANI/MWCNT (0.25 wt. %)	0.22	
PANI/MWCNT (8 wt. %)	3.32	
PANI	6.25	[104]
PANI/MWCNT (5 wt. %)	17.54	
PANI/MWCNT (10 wt. %)	20.66	
PANI/MWCNT (15 wt. %)	23.10	
PANI/CNT (1 : 1)	10.00	[105]
PANI/CNT (2 : 1)	6.67	
PANI/CNT (4 : 1)	1.72	
PANI/CNT (8 : 1)	0.41	
PANI	0.028	[106]
PANI/carboxylated CNT (1 wt. %)	0.126	
PANI/carboxylated CNT (6 wt. %)	6.154	
PANI/carboxylated CNT (7 wt. %)	3.349	

Other properties of composites with PANI also depend on the CNT content. A change in the dielectric properties of the material is observed with increasing concentration of single-walled CNTs [107]. The relaxation process, analyzed using the Kohlrausch-William-Watts (KWW) model, is found to occur at lower nanofiller loadings, but gradually decays as the number of SWCNTs increases, yielding relaxation spectra that gradually resemble those of a pure conductor. In addition, the competing processes between the effects of electrical percolation and interfacial capacitance are found to be inherently dependent on the carbon filler content.

In the literature, there are few results of studies of the mechanical properties of PANI composites with carbon nanotubes. Materials testing demonstrated an increase in tensile stress by 150 % and Young's modulus by 110 % when 2 wt. % CNTs were added to the polymer [108]. Huang J. et al. report that the tensile strength of PANI/CNT film composites increases significantly to 232.3 MPa, which is more than twice the tensile strength of carbon nanomaterial (67.2 MPa). The increased tensile strength of the composites can be attributed to the interfacial adhesion between the carbon nanotube film and PANI, promoting more efficient stress transfer [109].

One way or another, obtaining a CNT dispersion is an important stage in the production of PANI/CNT nanocomposite material by chemical polymerization. As indicated in a number of studies, covalent modification of CNTs with carboxyl [110] or sulfo groups [94] allows both to ensure the dispersibility of CNTs in water and to act as a matrix for the polymerization of aniline due to interaction with the monomer and the resulting PANI. In addition, after introducing acid groups, nanotubes can act as a modifying additive for PANI, which allows polymerization to be carried out in water without adding acid. However, it should be noted that polymerization in the absence of an additional modifying additive leads to the production of a nanocomposite material with a low degree of doping and, accordingly, low conductivity (about 10^{-2} S$\cdot$cm^{-1}) [94].

Pre-functionalized CNTs have been used to prepare PANI composites in other studies. Carboxylated multiwalled CNTs can be used as a dispersed carrier in a composite material demonstrating sensor sensitivity to ammonia [111]. Polyaniline was deposited onto the surface of multiwalled CNTs (MWCNTs) pre-oxidized in a mixture of nitric and sulfuric acids, and it was possible to obtain a composite with a specific surface area of 133.55 m$^2\cdot$g^{-1} and a specific capacity of 867 F$\cdot$g^{-1} [112]. Similarly prepared CNTs were used to obtain ternary CNT/PANI/ZnO composites, which have the ability to effectively absorb gamma radiation [113].

However, CNT functionalization does not always have a positive effect on the properties of composites. There are results indicating that pre-oxidation of CNTs contributes to a decrease in the conductive properties of the material [80]. There is no contradiction in these data, since most studies did not take into account the content of functional groups in CNTs. Dyachkova T.P. and colleagues were the first to analyze the influence of the method and degree of preliminary functionalization of carbon nanotubes on the process of oxidative polymerization of aniline [114]. A correlation has been established between the maximum value on the temperature curve of this reaction and the yield of its target product with the depth of preliminary oxidation of CNTs. The nature of the dependence of the electrically conductive properties of composites and the value of their specific surface area on the degree of preliminary functionalization of CNTs with carboxyl groups is shown. Composites based on carboxylated CNTs with a degree of functionalization of 0.2 mmol$\cdot$g^{-1} have the best electrical conductivity (3 S$\cdot$cm^{-1}). Materials with the maximum specific surface area (more than 170 m$^2\cdot$g^{-1}) were obtained using CNTs oxidized with concentrated nitric acid as a substrate for the deposition of PANI.

Based on the results of calculations obtained by molecular dynamics methods, a mechanism for the modification of carboxylated CNTs with PANI was proposed [115]. It has been shown that phenazine nucleates during the oxidative polymerization of aniline are formed on the surface of nanotubes, desorbed into the bulk of the reaction mixture, where PANI macromolecules then grow.

4.2. PANI / graphene composites

Over the past decade, graphene, which consists of a single layer of sp^2-hybridized carbon atoms linked into a hexagonal two-dimensional crystal lattice, has attracted enormous research attention as a functional material. This is due to its high electrical and thermal conductivity, high mechanical strength and high specific surface area [116–123]. In particular, its structure and unique electron transport properties make graphene in combination with a conducting polymer (for example, PANI) a promising material for the manufacture of electronic, electrochemical and optoelectronic devices [124–126].

Nanocomposites of PANI with graphene and its derivatives can be obtained in various ways, for example, chemical oxidative polymerization [127, 128], electrochemical oxidative polymerization [129, 130], interfacial polymerization [131], by mixing the starting components (polymer and graphene material) [132, 133].

The efficiency and simplicity of the method of chemical oxidative polymerization of aniline on the surface of graphene has made it the most common method for preparing PANI/G nanocomposites. It is reported that when using this approach to improve the electrochemical characteristics of composites and reduce the proportion of PANI in the volume of the reaction mixture, it is advisable to pre-functionalize the surface of graphene materials either with organic molecules or oxygen-containing functional groups. Thus, additional centers for polymer growth will be created on the surface of the carbon material [134]. Synthesis conditions and the percentage of polymer and carbon material in the final product affect the morphology of PANI/G composites. It has been reported that various nanostructures have been obtained: nanospheres [128], nanofibers [135, 136] or nanotubes [137].

The oxidative polymerization method can also be used to coat other carbon nanostructures, for example, mesoporous carbon, with PANI [138].

Methods for electrochemical oxidative polymerization of aniline in the presence of hafen are divided into potentiostatic [139] and potentiodynamic methods [134].

A distinctive feature of interfacial polymerization is that the aniline monomer is dissolved in organic solvents (for example, chloroform, benzene), and the oxidizing agent is dissolved in an aqueous acid solution. After transferring the prepared solutions into the reactor, an organic solvent/water interface is formed, at which the polymerization reaction occurs [131]. As a result of this approach, the PANI/G composite, which comes in the form of a composite film that can be easily separated, is formed at the interface [140].

It is also possible to obtain PANI-graphene composites by mixing and sonicating a dispersion of graphene material with previously prepared PANI [132–134]. The disadvantage of this approach is the instability of composites and their tendency to phase separation [132]. This drawback was eliminated by activating the graphene surface with the formation of acid chloride groups that interact with PANI [132–134].

4.3. Hybrid composites

In addition to binary PANI composites, the preparation of materials combining PANI, CNTs, graphene structures and other types of carbon materials has also been reported. The use of such combinations makes it possible to eliminate the disadvantages of individual dispersed carriers and, in some cases, achieve synergistic effects on various properties.

Graphene/carbon nanotubes/PANI composite can be used as a supercapacitor electrode material, which has a high specific capacitance (1035 $F \cdot g^{-1}$) and retains up to 94 % of the original capacity after 1000 charge/discharge cycles [141].

By combining a mixture of CNTs and graphene oxide with ready-made PANI and subsequent carbonization, a composite is obtained with the specific surface 176 $m^2 \cdot g^{-1}$ and the specific pore volume 0.232 $cm^3 \cdot g^{-1}$ [142].

Based on PANI-modified carbon nanotubes and graphene, a mesoporous airgel with a specific surface area of 289 $m^2 \cdot g^{-1}$ was obtained in a high-pressure autoclave in a supercritical isopropanol environment [143]. In this system, CNTs act as structure formers, preventing the agglomeration of graphene sheets, and PANI astices have a spherical shape. When using reduced graphene oxide and oxidized CNTs to form an airgel, it is possible to obtain a material with a higher specific surface area of 315 $m^2 \cdot g^{-1}$ [144].

Natural carbon materials are often used as one of the components of hybrid composites. For example, the authors of [145] obtained a stable porous sorbent by combining PANI, multi-walled carbon nanotubes and chitosan cryogel. To obtain a flexible composite with a developed surface, porous wood was used, on the surface of which a layer of electrically conductive CNTs was deposited, after which the surface of the material was coated with PANI in situ [146]. A flexible supercapacitor based on this composite has a high specific capacity of 45.89 $F \cdot g^{-1}$ at a current of 0.2 $A \cdot g^{-1}$; after 1000 charge-discharge cycles, about 99% of the capacity is retained; in addition, even when bent by 120°, 62.9 % of capacity is retained. By introducing PANI into a conductive network based on a hybrid material "nanocellulose – multiwalled carbon nanotubes", a film airgel electrode with a specific capacitance of the order of 2176.3 $mF \cdot cm^{-2}$ was obtained [147].

5. Application of PANI and composites based on it

PANI and its composites are of great interest for various fields of application due to the availability of fairly simple methods for their preparation and the possibility of synergistic effects when combining a dopant and PANI. Recently, most attention has been paid to the production of composites for use as electrode materials for supercapacitors, sorbents, and radiation-absorbing materials (Table 3).

As discussed above, PANI comes in a variety of forms, each with its own properties and applications. Leucoemeraldine, a fully reduced form of PANI, has found applications in electrochromic devices and lithium polymer batteries. Emeraldine salt, which is highly electrically conductive, is used in the sensor industry as an electromagnetic shielding material, in electrochromic devices, and as an electrode material in batteries. Some gas sensors are made using emeraldine salt. Pernigraniline is used in nonlinear optics [160, 161].

Composites based on PANI have high stable electrical conductivity and capacitance (up to 4800 $F \cdot g^{-1}$ [162]) (Table 4). It has also been established that the entire volume of material is involved in storing the charge. This sets this polymer apart from other conductive materials in which charge storage occurs only on the surface. Therefore, composites with PANI can be successfully used as materials for chemical current sources and supercapacitors. For these purposes, binary and three-component composites are being developed that combine PANI, carbon nanomaterials, and metal oxides [163, 164].

The ability of PANI and composites based on it to absorb radiation (due to a combination of magnetic and dielectric properties) opens up prospects for the creation of radio-absorbing [175, 176] and electromagnetic interference shielding materials [177, 178].

PANI and materials containing it can prevent or slow down the oxidation of metal by atmospheric oxygen, which makes it possible to manufacture anti-corrosion coatings [179–181].

The possibility of using PANI in tissue engineering biosensing and targeted drug delivery has been reported [182, 183]. In addition, PANI is considered as a biocidal additive in the production of coatings that protect against viruses [184].

Moreover, composites based on PANI-modified carbon nanotubes can find wide application in electrochemical sensors, solar energy converters, and highly efficient sorbents for heavy metals, bacteria and viruses.

Let us give a number of examples. PANI/CNT composites are proposed to be used in sensors for ammonia detection [185–187]. The detection mechanism is regulated by deprotonation of the emeraldine salt of PANI by NH_3 molecules and conversion to the emeraldine base of PANI, which leads to an increase in electrical resistance. It has been shown that temperature has a strong influence on the performance of sensors. The introduction of CNTs into the composite reduces this effect.

Table 3. Application areas of composites based on PANI and carbon nanomaterials

No.	Composite	Application	Source
1	PANI/ MWCNT	Electrode materials for supercapacitors	[148]
2	PANI/G	Electrode materials for supercapacitors	[149]
3	PANI/GO/G	Electrode materials for supercapacitors	[150]
4	PANI/regenerated exhaust gas	Electrode materials for supercapacitors	[151]
5	PANI/porous carbon microspheres	Electrode materials for supercapacitors	[152]
6	PANI/GO PANI/CNT	Sorbents	[153]
7	PANI/GO/CNT	Sorbents	[154]
8	PANI/regenerated exhaust gas	Sensors for temperature, relative humidity, pesticide detection	[155]
9	PANI/carboxylated CNTs	Biosensors	[156]
10	PANI/ MWCNT/ STARCH	Biosensors	[157]
11	PANI/CNT/Gold nanoparticles	Sensors for detecting zinc, lead and copper	[158]
12	PANI/CNT	Microwave absorbing materials	[159]

Table 4. Specific capacity and stability of PANI and its composites

No.	Composite	Specific capacitance, $F \cdot g^{-1}$	Current ($A \cdot g^{-1}$) or scan rate ($mV \cdot s^{-1}$)	Capacitance conservation	Source
1	PANI/CNT/MoS_2	350	10 $A \cdot g^{-1}$	68 % after 2000 cycles	[165]
2	PANI/GO/MoS_2	815	10 $mV \cdot s^{-1}$	93 % after 100 cycles	[166]
3	PANI/GO/TiO_2	713	10 $mV \cdot s^{-1}$	94 % after 100 cycles	
4	MWCNT	30	0.4 $A \cdot g^{-1}$	–	[167]
5	PANI	210	0.4 $A \cdot g^{-1}$	–	
6	PANI/MWCNT/TiO_2	270	0.4 $A \cdot g^{-1}$	67 % after 6000 cycles	
7	PANI/MWCNT/$Ni(OH)_2$	1917	1.0 $A \cdot g^{-1}$	75 % after 1000 cycles	[168]
8	PANI/polyndol (2:1)	682.4	0.5 $A \cdot g^{-1}$	78.6 % after 1000 cycles	[169]
9	PANI/polyndole/MWCNT (3 wt. %)	895	0.5 $A \cdot g^{-1}$	97.8 % after 1000 cycles	
10	PANI/CNT/graphene	415	3 $A \cdot g^{-1}$	96 % after 5000 cycles	[170]
11	PANI/graphene	310	3	74 % after 5000 cycles	
12	PANI/CNT	215	3	84 % after 5000 cycles	
13	PANI/reduced GO/Fe_3O_4	486.5	1	52.1 % after 2000 cycles	[171]
14	PANI/sulfonated graphene/NiO	1350	1	92.23 % after 5000 cycles	[172]
15	PANI/GO/MWCNT	696	20 $mV \cdot s^{-1}$	–	[173]
16	PANI/GO/$CoFe_2O_4$	781.27	1 $mV \cdot s^{-1}$	79.03 % after 5000 cycles	[174]

PANI composites with reduced graphene oxide have been used to fabricate a VOC sensor that exhibits high sensitivity towards methanol gas [188]. To detect nitrite in tap and rain water, an electrode modified with a reduced graphene oxide/$MnFe_2O_4$/PANI composite was developed [189].

Electrically conductive PANI/CNT composites have found application in the creation of various electrochemical enzyme sensors: sensors for the detection of ascorbic acid [190], glucose [191], phenolic compounds [192], pesticides [193], and cholesterol [194]. A sensor based on PANI and graphene oxide was developed to determine cortisol in human saliva [195].

The possibility of using PANI/CNT composites in solar cells was studied [196, 197]. It was shown that the performance of solar cells increases as a result of using a PANI/CNT composite. The increase in conversion efficiency is explained by more efficient charge transfer due to suppression of the charge recombination process [198].

Composite adsorbents consisting of PANI and carbon nanomaterials are increasingly considered as promising materials for water purification due to their ability to sorb various types of pollutants [199–201]. The prospects for using PANI as an adsorbent are due to the presence of adsorption centers, which are amine and imine groups that interact with pollutants in aqueous solutions [202].

It was shown that PANI/CNT composites can be used for the sorption of copper and nickel ions from water [203]. At the same time, deprotonation of PANI has little effect on this process, and the conversion of the modifying layer of PANI into the leucobase form upon reduction with hydrazine sharply increases the sorption capacity of the material for copper ions. PANI/CNT and PANI/GNP composites can be used for the sorption of various pollutants and pathogenic microorganisms [204], and the successful use of PANI/CNT composites for the extraction of scandium ions from aqueous media has been reported [205].

Hybrid composites based on mixtures of CNTs and graphene materials embedded with PANI demonstrate high sorption capacity with respect to zinc ions (346 $mg \cdot g^{-1}$ at pH 6.5) [142] and lead (350 $mg \cdot g^{-1}$) [143] and others heavy metals [144].

Some sources report quite unusual applications of PANI-based composites. PANI-modified graphene nanoplatelets were used as a reinforcing filler for a composite based on highly oriented ultra-high molecular weight polyethylene (UHMWPE) [206, 207]. It was found that PANI helps to reduce the aggregation of GNP in the polymer matrix and increase the degree of its crystallinity. The new lamellar crystal structure has high stretchability. The highest tensile strength of 1330 MPa has a composite containing 2 wt. % GNP/PANI filler, and the highest value of Young's modulus of 41 GPa is observed at 1 % content of the modified filler.

6. Conclusion

In this review, we have shown the promise of using PANI and its composites with carbon nanomaterials in various industries due to their unique electrical, physical, chemical, and optical properties. Recent studies show that combining PANI with various substances (carbon nanotubes, graphene, graphene oxide, metal oxides) can improve the performance characteristics of the polymer.

However, despite numerous studies and positive results, many challenges still need to be overcome on the path to commercialization of composites. The analyzed studies are devoted to the development of new materials of complex composition, the study of their properties, and specific proposals for practical use.

A generalization of scientific results shows that the selection of the optimal composition of composites remains relevant in order to find ways to increase their electrical capacity and cyclic stability, increase electrical conductivity and specific surface area. For this purpose, materials are developed that consist of three or more components. And obviously, by varying their mass ratio, fundamentally different materials can be obtained. It has been shown that the properties of composites with PANI depend on the presence of functional groups on the CNM surface. Although such information is available in the literature, it is scattered and requires additional study.

It is assumed that in the near future, composites being developed with PANI may become the basis of many technologies that provide a high-quality standard of living (ecology, energy, safety), but for this it is necessary to continue scientific research. Thus, it is necessary to establish what effect functional groups on the surface of carbon nanomaterials have on the performance characteristics of composites. To evaluate the effectiveness of composites, it is necessary to test them in practice, and for further commercialization it is necessary to develop protocols/recommendations that include a description of methods for obtaining composites with a given structure and properties.

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8. Conflict of interests

The authors declare no conflict of interests.

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Information about the authors / Информация об авторах

Irina V. Gutnik, Cand. Sc. (Eng.), Associate Professor, Tambov State Technical University (TSTU), Tambov, Russian Federation; ORCID 0000-0003-1236-7187; e-mail: i.v.gutnik@yandex.ru

Tatyana P. Dyachkova, D. Sc. (Chem.), Professor, TSTU, Tambov, Russian Federation; ORCID 0000-0002-4884-5171; e-mail: dyachkova_tp@mail.ru

Elena A. Burakova, D. Sc. (Eng.), Associate Professor, TSTU, Tambov, Russian Federation; ORCID 0000-0001-8927-7433; e-mail: elenburakova@yandex.ru

Evgeniy N. Tugolukov, D. Sc. (Eng.) Professor, TSTU, Tambov, Russian Federation; ORCID 0000-0003-1766-3786; e-mail: tugolukov.en@mail.ru

Artem V. Rukhov, D. Sc. (Eng.), Head of the Department “Chemistry and Chemical Technologies”, TSTU, Tambov, Russian Federation; ORCID 0000-0001-9194-8099; e-mail: artem1@inbox.ru

Georgiy A. Titov, Student, TSTU, Tambov, Russian Federation; ORCID 0000-0002-3930-0559; e-mail: bombercd1@mail.ru

Гутник Ирина Владимировна, кандидат технических наук, доцент, Тамбовский государственный технический университет (ТГТУ), Тамбов, Российская Федерация; ORCID 0000-0003-1236-7187; e-mail: i.v.gutnik@yandex.ru

Дьячкова Татьяна Петровна, доктор химических наук, профессор, ТГТУ, Тамбов, Тамбов, Российская Федерация; ORCID 0000-0002-4884-5171; e-mail: dyachkova_tp@mail.ru

Буракова Елена Анатольевна, доктор технических наук, доцент, ТГТУ, Тамбов, Российская Федерация; ORCID 0000-0001-8927-7433; e-mail: elenaburakova@yandex.ru

Туголуков Евгений Николаевич, доктор технических наук, профессор, ТГТУ, Тамбов, Российская Федерация; ORCID 0000-0003-1766-3786; e-mail: tugolukov.en@mail.ru

Рухов Артем Викторович, доктор технических наук, профессор, заведующий кафедрой, ТГТУ, Тамбов, Российская Федерация; ORCID 0000-0001-9194-8099; e-mail: artem1@inbox.ru

Титов Георгий Анатольевич, студент, ТГТУ, Тамбов, Российская Федерация; ORCID 0000-0002-3930-0559; e-mail: bombercd1@mail.ru

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