

GRAPHENE COMPOSITES WITH HYDROGEL

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Composites are multiphase materials consisting of two or more different materials with different properties that are firmly bound to each other on the surface. As new nanomaterials, graphene and graphene oxide are particularly interesting due to their ability to form composites and nanocomposites with hydrogels. Graphene has attracted a lot of attention. Hydrogels are materials that have a three-dimensional structure, capable of absorbing a large amount of surrounding fluid without dissolving. Stimuli-sensitive hydrogels can change a physical property in response to external stimuli. Hydrogels based on monomers such as *N,N*-diethylacrylamide, and *N*-(2-hydroxyethyl) acrylamide exhibit great scientific and technological importance. They have found application in the paint and varnish industry, the pharmaceutical, cosmetic, food industry, agro-industry, and textile industries. Previous research has proven that graphene significantly boosts the electrical, thermal, and mechanical properties of hydrogels. Hydrogelcomposites with graphene have a porous structure. The paper represents a literature overview of methods for the synthesis and characterization of synthesized hydrogels and hydrogel composites with graphene and graphene oxide.

Keywords: composite, graphene, hydrogel, synthesis

Introduction

Composite materials consist of two or more different materials that are firmly bound to each other at the interface, and form regions large enough to be regarded as continua. There are two types of major characteristics that determine the properties of composite material: the internal phase geometry, ie. phase interface geometry, and phase physical properties, ie. their constitutive relations. The first one is much more difficult to classify than the second one since the internal geometry of each composite material is somewhat random [1].

Graphene is a material with many advantages. It is the thinnest and strongest known material, whose charge carriers show enormous internal mobility. It can maintain a current density six times that of copper, exhibiting record thermal conductivity and stiffness ($\sim 3,000 \text{ W m}^{-1}\text{K}^{-1}$ and 1,060 GPa, respectively). These great properties of graphene sheets can be used for creating composite material [2]. In addition to being a precursor in graphene synthesis, graphene oxide (GO) can also be used as a phase composite material, also with outstanding graphene properties [3].

Polymers that have a three-dimensional network in their structure, and a high degree of flexibility, are called hydrogels. Because of their soft, rubbery consistency similar to living tissue, and outstanding physical properties, they are

capable of absorbing a large amount of surrounding fluid without dissolving [4].

Graphene significantly improves the electrical, mechanical, and thermal properties of traditional polymer hydrogels. Namely, graphene has two roles in hydrogels. First, it is considered as a gelator for incorporation into hydrogels and then, as a filler for mixing with small molecules and macromolecules for the preparation of multifunctional hydrogels, which are collectively called graphene-based hydrogels [5].

The paper presents a literature review of composite materials of graphene and graphene oxide with hydrogels, and different ways to synthesize hydrogels and hydrogel composites with graphene and graphene oxide. We aim to present various methods for the synthesis and characterization of *N,N*-diethylacrylamide and *N*-(2-hydroxyethyl)acrylamide as a potential monomer in the synthesis of hydrogels.

Composite materials

Composite materials belong to the class of the most diverse and most important materials whose use and purpose are expanding rapidly. They offer unique possibilities due to combining several materials [6]. They are more cost-effective and a better replacement for conventional materials since their structural performance is

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much more versatile than the one achieved with conventional materials. Such versatility can be used in the design of the required material through a complete analysis of the individual materials that make up a given composite. By analyzing the material, we can assume the structural behaviour of the composite itself [7]. Thus polymeric materials have found great application. Among others, graphene can be incorporated directly into polymers. Because of an efficient load transfer between the graphene, or graphene oxide, film, and the polymer these composite materials show excellent mechanical properties. In the range of 62%- 76%, composite material at a weight ratio of graphene oxide of 0.7%, increases Young's modulus and Tensile strength. The graphene-hydrogel composite showed an electrical conductivity of $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at a graphene volume percentage of 2.0% [8].

Graphene

Nanoparticles (NP) are particles whose size does not exceed 100 nm. The use of nanoparticles has given an enormous efficiency compared to the large mass particles due to their large specific surface area, different functionalities, the presence of active sites on the surface [9], extremely high stability, and high adsorption capacity [10]. It is a fact that many systems behave differently at the nano level. They are functionally more useful and, thus, more commercially and scientifically applicable. Graphene is the thinnest known material, with a thickness of one atom. Its weight of approx. 0.77 mg per 1 m^2 makes it the lightest known material. Graphene is also the strongest known material, stronger than steel, with a fibres strength of 150,000,000 psi and a tensile strength of 130,000,000,000 Pa. It is both the best thermal and, the best electrical conductor. An important characteristic of graphene is its optical light absorption. In graphene, the carbon atoms of sp^2 are hybridized, as a result of which it has a Ravan structure. Within the graphene plane, each carbon atom establishes three strong covalent bonds, at an angle of 120° , with the three nearest carbon atoms, thus forming a benzene ring. Covalent or sigma (σ) bonds are formed in the presence of three valence electrons from 2s, $2p_x$, and $2p_y$ atomic orbitals, where the length of these C-C bonds is 0.142 nm. Benzene rings are further densely packed in a two-dimensional (2D) crystal lattice in the graphene plane, forming a graphene layer with a honeycomb structure. The fourth valence electron does not participate in covalent bonding, it is located in the $2p_z$ orbital which is oriented normally to the graphene plane forming a π bond. It does not lie in the same plane as the σ -bond, but consists of two spatial parts, one of which is above and the other below the plane of the σ -bond. Depending on the arrangement and orientation of the carbon atoms in the benzene ring that form the basis of the graphene plane, the edges of graphene have a stoic or zigzag configuration [11]. The type of graphene edge greatly affects the electrical properties of the graphene layer [12] and thus the application possibilities. Graphene may contain one, two, or more

layers (3 to 10) stacked on top of each other and interconnected by weak Van der Waals forces [13, 14].

Hydrogels

Hydrogels are polymeric compounds. Hydrophilic monomers linked by physical bonds (hydrogen, dipole-dipole, electrostatic attraction, ionic interactions) or chemical bonds (covalent crosslinking) form a three-dimensional network. Hydrogel networks can be constructed of one or more monomers, when we talk about homo- or copolymer hydrogels, respectively [15]. The specificity of hydrogels lies in their ability to bind large amounts of surrounding fluids thanks to crosslinking-while remaining insoluble. Polymer hydrogels are "soft materials" that can change volume and shape in correlation to external stimuli (electric or magnetic field, light, temperature and pH, radiation, enzymes). Compared to other synthetic biomaterials, hydrogels are most reminiscent of natural living tissue, thanks to their very structure, soft consistency, and high content of absorbed fluid [16]. The high content of absorbed fluid and soft elastomeric nature lead to minimal mechanical irritation and friction of the surrounding tissues, as well as, enables biocompatibility. Different types of monomers have been used in the synthesis of hydrogels. The choice of monomers and synthesis conditions lead to certain properties and behavior of hydrogels. They affect swelling, stability itself, biodegradability, mechanical strength, and biocompatibility. Acrylic and methacrylic acid monomers are often used [17]. The hydrophilicity of such hydrogels can be increased by the inclusion of ether groups, while there is extensive data on monomers containing an amide functional group [18]. Polymerization of acrylamide-based hydrogels, through monomers in solution, can be prepared using a crosslinker or using γ radiation [19]. Crosslinking of monomers can be performed using post-polymerization, radiation crosslinking, or using crosslinking agent [20]. Eid [21] synthesized the hydrogel by radiation copolymerization of *N*-vinylpyrrolidone to acryl acid by radiation. The amount of grafted polyvinylpyrrolidone (PVP) depends on the radiation dose and dose intensity, as well as on the temperature and duration of the copolymerization itself.

Multifunctional monomers are used in co-crosslinking by thermal initiation. The crosslinking agents most commonly used are divinyl monomers. The most used group of monomers is the one where there are two vinyl groups. Several networking agents have been reported, among which ethylene glycol dimethacrylate [22]. *N,N*-methylenebisacrylamide is often used as much as allyl methacrylate, hexamethylenebis-(methacryloyloxyethylenecarbamate), 2-hydroxy-trimethylenedimethacrylate, 2,3-dihydroxy-tetramethylene dimethacrylate, 1,1,1-tris (methacryloyloxy methyl) propane, 1,3,5-triacryloylhexahydrotriazine, methylene bis-(4-phenyl isocyanate), 2,2'-(*p*-phenylenedioxy) diethyl dimethacrylate and 3,3-tetramethylene-bis-(1-vinyl imidazolium diiodide) [20].

The use of hydrogels is diverse. They can be used as drug carriers [23], heavy metal sorbents [24] and colour sorbents [25]. Many hydrogels have found application in the release and/or adsorption of pesticides [26].

Hydrogels based on *N,N*-diethylacrylamide monomers Thermosensitive polymers, based on monomers such as *N,N*-diethylacrylamide (DEA), are scientifically and technologically important compounds, widely used in the pharmaceutical, cosmetic, food and paint industries. They can modify viscosity and rheology and encapsulate the active compounds; they are used as smart systems for the release of medicinal substances, but also pesticides [27]. Furthermore, they are used as smart textiles [28], in biomedicine [29], tissue engineering and regenerative medicine [30].

Many studies discuss poly (*N*-isopropylacrylamide), PNIPAM, as a pH and a thermo-sensitive polymeric material. Until recently *N*-isopropylacrylamide (NIPAM) has been very popular because of its characteristics and applicability. In pure water, the lower critical temperature of the solution (LCST) of NIPAM is about 32 °C [31]. Therefore, the characteristics and applicability of NIPAM-based polymeric materials have contributed to its popularity. On the other hand, bio-application of NIPAM is limited because in an aqueous solution, during hydrolysis, PNIPAM-based materials could release toxic amines [32]. Because of lower cytotoxicity hydrogels based on poly(*N,N*-diethylacrylamide) [33], PDEA, may be new attractive candidates for biomedical applications with an LCST of 25-33 °C [34-37]. However, conventional three-dimensional hydrogels also have some drawbacks, since they are brittle at room temperature, have poor mechanical properties, low swelling, and slow response rates [38]. On the other hand, compared to PNIPAM hydrogels, the degree of swelling of PDEA hydrogels is much lower due to the difference in chemical structure [39]. PDEA is a hydrogel that reacts to changes in pH and temperature, with low toxicity, high swelling, fast reaction, and good mechanical properties.

The behavior of PDEA in aqueous solutions is still the subject of many scientific studies. Polymers of this type undergo a thermally induced, reversible phase transition. The temperature at which this occurs is LCST [40, 41].

Semi-interpenetrating hydrogel polymer network (semi-IPN) can be synthesised using DEA as a monomer. Semi-IPN hydrogels are usually synthesized using simultaneous polymerization of crosslinked monomers [42, 43] and have a physically crosslinked network. This type of hydrogel can be pH or/and thermo-sensitive by introducing stimuli-sensitive monomers like acrylic acid [44], into a semi-IPN hydrogel. Hydrogels, synthesised in this way, have good thermal and mechanical properties and high response speed.

Using free radical polymerization Tuan and al. synthesized and characterized the poly(*N,N'*-dimethyl acrylamide-co-itaconic acid), P(DEA-co-IAM), copolymer [45]. They have changed the molar ratio of linear

copolymer P(DEA-co-IAM) to obtain pH and thermo-sensitive semi-IPN hydrogel. By characterization, it has been shown that the obtained hydrogel has a porous structure. Changing the ratio of copolymer pore sizes can be controlled. Compared to conventional hydrogel, the semi-IPN hydrogel has high elastic behaviour, thermal stability, and superior mechanical properties. With increasing IAM content, LCST of these copolymers is increased. The synthesis of DEA-based polymers can be performed by anionic polymerization. Anionic polymerization of *N,N*-dimethyl acrylamide (DEA) with 1,1-diphenyl-3-methylpentillithium (DPPLi) and diphenylmethylpotassium (Ph₂CHK) in the presence of triethyl borane (Et₃B) in tetrahydrofuran (THF) at 30 °C was performed by Kobayashi *et al.* [46]. At the temperature of 30 °C researchers synthesized hydrogels using post polymerization of DEA with Ph₂CHK/Et₃B with a heterotactic configuration that is highly syndiotactic. Isotactic polymers are formed in the absence of Et₃B. Chen *et al.* [38] prepared a semi-IPN hydrogel based on DEA, kappa-carrageenan (KC), and methacrylic acid (MA) by free radical polymerization. Following the synthesis of kappa-carrageenan-g-poly(methacrylic acid)/ poly(*N,N'*-diethylacrylamide), KC-g-PMA/PDEA researchers studied the effect of changes in temperature and pH on the swelling degree of hydrogels. They came to the conclusion that with increasing content of KC-g-PMA, the swelling degree also increases. It was 4.94 g·g⁻¹ within 150 minutes, about 7.63 g·g⁻¹ within 450 minutes, while the swelling degree of the various test samples was for semi-IPN1, semi-IPN2, semi-IPN3 and semi-IPN4 about 5.60, 6.19, 7.31 and 16.67 g·g⁻¹ within 150 minutes, and about 10.04, 12.56, 16.16 and 31.03 g·g⁻¹ within 450 minutes, respectively. The porous structure of hydrogels plays an important role and leads to faster swelling because it enables easy transfer of water molecules between the hydrogel network and the outer aqueous phase. During the swelling process, the pores of the semi-IPN hydrogel gradually increase, which could lead to an accelerated absorption. For semi-IPN hydrogels, due to the existence of KC-g-PMA, water molecules can easily diffuse into the hydrogel network and polymer chain expansion can easily occur [47]. The increase in KC-g-PMA content improved the thermo- and pH sensitivity of the hydrogel. In glass tubes using free radical polymerization reactions of poly (2-dimethylamino) ethyl methacrylate/poly(*N,N'*-diethylacrylamide), PDMAEMA/PDEA at 15 °C for 24 Zhang *et al.* synthesized semi-IPN hydrogels. In the semi-IPN hydrogel structure, high molecular weight chains act as channels for water movement. Crosslinking density of hydrogels affects on swelling kinetics. By changing the content of copolymer, researchers can control swelling kinetics of hydrogels. Delaitre *et al.* performed free radical polymerization of poly(*N,N'*-diethylacrylamide) [47]. In addition to DEA, Bloc Builder (151.4 mg, 397 mmol) and *N*-tert-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)]nitroxide, SG1 were used. After characterization of poly (*N,N'*-diethylacrylamide) (PDEA), Idziak *et*

al. [35] reported that the LCST of PDEA, prepared by radical polymerization, was about 33 °C. Lessard et al. [48] examined the dependence of molecular weight on LCST poly(*N,N'*-diethylacrylamide) on 11 samples of polymers with an average molecular weight (M_n) ranging from 9.6×10^3 to 1.3×10^6 g·mol⁻¹. Using microcalorimetry and turbidimetry researchers investigate LCST polymer values. They found the inverse dependence of LCST on molar mass. It has been concluded that if the molar mass of the hydrogel change, then LCST, enthalpy and entropy change, too. This is especially noticeable in the low molecular weight range. For isotactic PDEA hydrogel with low molar masses ($M_n < 5000$ g·mol⁻¹), the transition temperature was 10 °C higher than for their syndiotactic homologues [49].

Table 1. Substances used in synthesis, synthesis techniques and characterization applied in papers, values of swelling and LCST hydrogels.

Monomer	Initiator	Crosslinker	Synthesis technique	Characterization methods	Swelling degree, α , (g·g ⁻¹)	LCST, (°C)
DEA, IAM,	APS, TEMED	MBA	free radical polymerization in aqueous solution	FTIR, ¹ H NMR, DSC, SEM, TGA, DLS, GPC	43,44	31,3- 33,4
DEA, Ph ₂ CHK, Et ₃ B,	DPPLi		Anionic polymerization	TGA, SEM, ¹³ C NMR	Swell in benzene	
DEA, KCMA	APS	MBA	free radical polymerization	FTIR, SEM	31,03	28
PDMAEMA, DEA	APS	MBA	free radical polymerization	FTIR, SEM, DSC	30,55	31
DEA	SG1	BlocBuilder	free radical polymerization	¹ H NMR, SEC, SEC/ESI-MS LXQ		32- 33
DEA	AIBN		free radical polymerization	UV, DSC, Gel permeation chromatography		33
DEA	C(MA) _n		GTP	SEC, ¹ H NMR, HPLC		
Pektin, DEA	CAN		microwave-induced graft copolymerization	¹³ C-NMR, DSC/ TGA, XRD, SEM		31
SA, DEA	AIBN		Microwave-initiated free radical polymerization	FTIR, ¹³ C-NMR, DSC, TGA, XRD, SEC, SEM		

Star-shaped polymers as an example of branched polymers [50] are widely accepted as thermosensitive polymers [51] carriers of medicinal substances [52], and biomedical materials [53]. In a structure, they have a central core connected to several linear chains (arms) [54]. Using catalysed group transfer polymerization (GTP) Li et al. synthesized poly(*N,N'*-diethylacrylamide). In the form of a nucleus they use B (C₆F₅)₃, ethyldimethylsilane (EtMe₂SiH) as hydrosilylan [55]. By microwave-induced copolymerization of DEA Işık and Tokmak [56] modified pectin. They also use cerium ammonium nitrate (CAN) and *N,N,N',N'*-tetramethylethylenediamine

(TEMED). Infrared Fourier transformer (FTIR), nuclear magnetic resonance (¹³C-NMR), differential scanning calorimetry with thermogravimetric analysis (DSC/TGA), X-ray spectroscopy (XRD), and scanning electron microscopy (SEM) were used to verify the structure of the verifiers. UV spectroscopy is used to determine the LCST of the grafted hydrogel. Grafted hydrogels were found to show high heat resistance and to have been thermosensitive, with a LIST of 31 °C. Akin et al. also synthesized copolymers that have DEA in their structure by microwave polymerization [57].

The substances used in the synthesis, the synthesis techniques and characterization methods, the swelling degree, and LCST hydrogels in reviewed papers are shown in Table 1.

Hydrogels based on *N*-(2-hydroxyethyl)acrylamide monomers

Hydrophilic poly (*N*-(2-hydroxyethyl) acrylamide) (PHEAA) is an antibacterial material that has been widely investigated [58,59]. In recent years, hydrogels with good biocompatibility have attracted much attention in bio-devices, but most of them lack eminent mechanical properties that greatly limit their practical application. Zhang et al. [60] have synthesized a new hybrid, ionic, covalently crosslinked double network (DN) hydrogels, using a simple method based on sodium alginate (SA) and antibacterial *N*-(2-hydroxyethyl) acrylamide (HEAA). Synthesized hydrogels using this method have great antibacterial and mechanical properties. The polymerization was performed under ultraviolet (UV) light at 365 nm for 6-8 hours to form a composite hydrogel P (HEAA/SA). The hydrogels were further placed in 0.3 M calcium chloride solution for 2 hours yielding ion-covalently crosslinked PHEAA/SA-Ca²⁺ hydrogel. After testing and characterization of DN hydrogels, it was concluded that it has an excellent tensile strength (1.32 MPa), high modulus of elasticity (0.31 MPa), pronounced fatigue resistance, and good antibacterial properties, as high in vitro compatibility.

Due to its characteristics, long-term stability, and biocompatibility of PHEAA, Zhao et al. [61] synthesized stable and, pH-sensitive hydrogels of poly(*N*-(2-hydroxyethyl)acrylamide-acrylic acid), P(HEAA/AA) with good biocompatibility and drug delivery. They performed free copolymerization [62] using inverse microemulsion free radical polymerization. PHEAA and P (HEAA/AA) nanogels were prepared by the inverse microemulsion polymerization method [63]. Wang et al. [64] synthesized different types of branched polymers, spherical diblock polymer brushes. Like core, they use polystyrene with photoinifer (PSV). They were also prepared by surface-initiated photoinifer-mediated polymerization (SI-PIMP) and used in different order poly(acrylic acid)-b-poly(*N*-(2-hydroxyethyl) acrylamide) (PSV@PAA-b-PHEAA) and poly(*N*-(2-hydroxyethyl)acrylamide)-b-poly(acrylic acid), (PSV@PHEAA-b-PAA). Then the characterization of synthesized hydrogels has been done. It is necessary

to find a new biomaterial for biomedical devices with excellent stability, durability and biocompatibility. By radical polymerization of surface-initiated atom transfer (SI-ATRP) Zhao et al. [66] synthesized and characterized PHEAA on gold surfaces and gold nanoparticles (AuNP) to form a stable antimicrobial coating (against covering solid surfaces with plant and animal organisms) that resists bacterial binding and protein adsorption. Using surface plasmon resonance (SPR) researchers show that all PHEAA brushes coated on a gold substrate, from undiluted blood plasma and serum can achieve almost zero adsorption of protein.

An overview of the substances used in the synthesis of hydrogels based on *N*-(2-hydroxyethyl) acrylamide, the synthesis techniques and characterization used by the researchers, the swelling degree, and LCST hydrogels in the papers are provided in Table 2.

Table 2. Overview of substances used in the synthesis of hydrogels based on *N*-(2-hydroxyethyl)acrylamide, synthesis techniques and characterization, swelling degree and LCST of hydrogels

Monomer	Initiator	Crosslinker	Synthesis technique	Characterization methods	Swelling degree, $\alpha, g \cdot g^{-1}$
SA, HEAA	α -ketoglutaric acid	MBA	UV polymerization	inverted fluorescent microscope	5,7
HEAA, AA	ω -mercaptoundecyl bromoisobutyrate	MBA	inverse microemulsion free radical copolymerization	UV-vis, 1H NMR, TEM, AFM	
PS, AA, HEAA	Photoiniferter		emulsion polymerization, surface-initiated photoiniferter-mediated polymerization	FTIR, TEM, DLS	

Graphene composites with hydrogel

Graphene and graphene oxide are particularly interesting in the field of polymeric materials specifically because of their ability to form composites and nanocomposites with hydrogels, giving them outstanding properties [67]. The inclusion of nanoparticles in polymer blends has led to a revolutionary goal due to the improvement of the mechanical [68], and thermal and biological properties of the polymer matrix of hydrogels [69]. Non-equilibrium morphologies of phase-separating mixtures can be captured to adjust their properties by the addition of nanoparticles. Nanoparticles also promote the suppression of unfavourable enthalpy and entropy interactions between mixture components, which changes the domain morphology and interaction parameter [70].

Nanocomposites with graphene cause faster colony shrinkage of *S. aureus* and *E. coli*, thus showing stronger antibacterial activity compared to pure hydrogels [71]. Graphene composites with hydrogels have a porous structure which enables adsorption testing when removing pesticides. The very structure of graphene hydrogel (GH) as a super adsorbent offers several new possibili-

ties in the adsorption of pesticides. Primarily thought of as a process that can be easily controlled, the synthesized composite contains hydrogen bonds that allow good adsorption of pollutants. The surface of GH is such that graphene agglomerates are unable to form, further favouring adsorption. One of the best features is the fact that the composite can be easily removed from purified using filtration or decantation [72].

Xavier et al. used the Hummer method to synthesize graphene oxide, with which they later made composites with hydrogels (polystyrene (PS) and polyvinyl (methyl ether), (PVME) were used as monomers) [73]. PS/PVME/GO composite material was prepared by shear mixing. The phase transition, LCST, and PVME in water were recorded at 37 °C [74]. Researchers from the University of Belgrade and Kyung Hee University synthesized a composite of hydrogel poly (vinyl alcohol) (PVA) and graphene doped with silver by in situ electrochemical syntheses. The addition of graphene in PVA hydrogels led to an improvement in their mechanical properties. In the next step, they examined the elastic properties of the composites because such material must be both tough and elastic [75]. Thermo- and pH-reactive composite networks of graphene oxide and poly (*N*-isopropylacrylamide-co-acrylic acid), (PNIPAM-co-AA) hydrogels were synthesized by researchers [74]. GO sheets were synthesized by a modified Hummer method while monodisperse microgels PNIPAM-co-AA were prepared by precipitation polymerization. Ma et al. also synthesized [75] 3D porous graphene composite with hydrogel by a safe and efficient hydrothermal reduction method [76]. Characterization of physicochemical properties of synthesizes granules was performed using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) method, transmission electron microscopy (TEM), and Raman spectrum. It has been proven that the composite has excellent adsorption capacity. Furthermore, it has been concluded that by reducing the size of hydrogels, the adsorption process can be accelerated. It seems that water, within the hydrogel, improves the adsorption performance of composites and also has excellent adaptability to environmental factors. Przekop *et al.* [77] present the possibilities of producing composites based on biodegradable polylactide (PLA) with the addition of graphite. The team synthesized composites with a share of graphite: 1%, 2.5%, 5%, 7.5% and 10%. The tribological, mechanical, and chemical properties of the mentioned materials were examined. After performing SEM observations of the samples before and after the friction test it has been shown that the increase in graphite content causes a significant reduction in wear. What is more, the addition of graphite significantly changed the mechanical properties. Heshmatpour et al. modified the nanohydroxyapatite/ graphene composite with synthetic polymers of polyvinylpyrrolidone and polyethylene glycol (PEG) [78]. The modification was also performed with a natural polymer, chitosan specifically. After pure nanohydroxyapatite (nHA) was synthesized, characterization

was performed using FTIR, X-Ray, scanning field emission microscopy (FESEM), and TGA thermogravimetric analysis [79]. Graphene-polymer composites found application in many different areas because of their excellent physicochemical properties. But their synthesis is still an extremely energy-intensive and environmentally unpleasant process. Polikatos and colleagues presented a more unique synthesis of water-based monolithic 3D composite structures of reduced graphene oxide (rGO) with polymer nanoparticles of poly(methyl methacrylate)- (PMMA) [80]. They developed a new method based on a self-installation process caused by reduction that is performed in mild conditions, using batch emulsion polymerization of a monomer mixture made of methyl methacrylate (MMA)/ glycidyl methacrylate (GMA) in a diameter of 90/10 wt.%. Because of existing of cross-linked bonds in composite structures, they have the resistance of solvents.

Table 3 comprises the substances used in the synthesis of graphene-hydrogel composites, methods of obtaining graphene, hydrogels, and graphene-hydrogel composites, as well as the characterization methods used in the reviewed papers.

Table 3. Overview of substances used in the synthesis of graphene- hydrogel composites, methods of obtaining graphene, hydrogels and graphene- hydrogel composites, as well as characterization methods used in the papers

Monomer	Graphene (graphene oxide) production	Synthesis technique of hydrogels	Synthesis of composites	Characterization methods
Ascorbic acid, GO	Hummers method	Ultrasonic polymerization	Thermosynthesis	FTIR, UV-vis, TEM, SEM, ESEM, XRD, BET
PS, PVME, graphite flakes	Hummers method	continuous mechanical mixing	shear mixing	FTIR, SEM, DSC, POM
Silver, PVA, Gr		Thermoinitiated free radical polymerization	Freezing and thawing technique	UV-Vis, Raman spectroscopy, FE-SEM, FTIR, XRD, CV, TGA
NIPAM, AA, GO	modified Hummers method	Precipitation polymerization	Networking GO sheets with PNIPAM- <i>ko</i> -AA	SEM, FTIR, Raman spectroscopy, XRD, TGA, DSC, UV-VIS
CS, PEG, GO, PVP			Ultrasonication	FTIR, XRD, EDX FESEM, TGA
rGO, PMMA		batch emulsion polymerization	Reduction reaction	SEM, BET, ¹³ C NMR, TGA/DSC

Conclusion

It is very important to create new, superior, smart materials that are widely used, more economical, and more environmentally friendly. Due to their structural performance, composite materials are becoming more and more interesting in the science of materials. By incorporating graphene into a three-dimensional network of hydrogels, its superior properties are also incorporated. The resulting composite material is characterized by excellent properties. Due to low cytotoxicity, pH, and thermosensitivity, the low critical temperature of the

solution, high level of swelling, fast reaction, and good mechanical properties, poly(*N,N'*-diethylacrylamide) is a good choice when choosing a monomer that will be part of the hydrogel. The monomer that has been widely researched due to its properties is the hydrophilic, antibacterial material poly (*N*-(2-hydroxyethyl) acrylamide). Composite materials of graphene and graphene oxide with hydrogels belong to the materials that have found application in many areas.

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Nomenclature

NP- nanoparticles,
 CNM-carbon nanomaterials,
 Gr- graphene,
 GO- graphene oxide,
 rGO- reduced graphene oxide,
 PVP- polyvinylpyrrolidone,
 DEA- *N,N'*-diethylacrylamide,
 PDEA- poly(*N,N'*-diethylacrylamide),
 NIPAM- *N*-isopropylacrylamide,
 PNIPAM- poly(*N*-isopropylacrylamide),
 LCST- Lower critical solution temperature,
 semi-IPN- semi interpenetrating polymer network of hydrogels,
 IAM- itaconic acid,
 P (DEA-co-IAM)- poly(*N,N'*-diethylacrylamide-co-itaconic acid),
 DPPLi- 1,1-diphenyl-3-methylpentyllithium,
 Ph₂CHK- diphenylmethylpotassium,
 Et₃B- triethylborane,
 THF- tetrahydrofuran,
 KC- kappa-carrageenan,
 MA- methacrylic acid,
 PMA-poly (methacrylic acid),
 KC-g-PMA/PDEA- kappa carrageenan-g-poly (methacrylic acid)/poly(*N,N'*-diethylacrylamide),
 PDMAEMA/PDEA- poly (2-dimethylamino) ethyl methacrylate/poly(*N,N'*-diethylacrylamide),
 SG1- *N*-tert-butyl-*N*-[1-diethylphosphono-(2,2 -dimethylpropyl)]nitroxide,
 AIBN- 2,2'-azobis-(isobutyronitrile),
 N₂-nitrogen,
 M_n - average molecular weight,
 EtMe₂SiH- ethyldimethylsilane,
 GTP- catalyzed group transfer polymerization
 CAN- cerium ammonium nitrate,
 TEMED- *N,N,N',N'*- tetramethylethylenediamine,
 FTIR- Fourier transform infrared spectroscopy,
 NMR- nuclear magnetic resonance,
 DSC- Differential scanning calorimetry,
 TGA- thermogravimetric analysis,

XRD- X-ray spectroscopy,
 SEM- scanning electron microscopy,
 FESEM- field-emission scanning electron microscopy,
 POM- polarized optical microscope,
 UV- ultraviolet spectroscopy,
 CV- Cyclic voltammetry,
 TEM- transmission electron microscopy,
 HEAA- *N*-(2-hydroxyethyl) acrylamide,
 PHEAA- poly (*N*-(2-hydroxyethyl) acrylamide),
 DN- double mesh hydrogel,
 SA- sodium alginate,
 PHEAA/SA- poly (*N*-(2-hydroxyethyl) acrylamide- sodium alginate)
 PHEAA/SA-Ca²⁺- hybrid ion-covalently crosslinked poly (*N*-(2-hydroxyethyl) acrylamide-sodium alginate),
 AA- acrylic acid,
 PSV- polystyrene with photoinferter,
 P (HEAA/AA)- poly(*N*-(2-hydroxyethyl) acrylamide-acrylic acid,
 SI-PIMP- surface-initiated polymerization mediated by photoinferter,
 Au- gold,
 AuNP- gold nanoparticles,
 SI-ATRP- radical polymerization of atomic transfer with surface initiation,
 SPR- surface plasmon resonance,
 GH- graphene hydrogel,
 PS- polystyrene,
 PVME- polyvinyl (methyl ether),
 PVA- poly (vinyl alcohol),
 BET- Brunauer-Emmett-Teller method,
 PLA- polylactide,
 nHA- nanohydroxyapatite,
 MMA- methyl methacrylate,
 PMMA- poly (methyl methacrylate),
 GMA- glycidyl methacrylate,
 CO₂- carbon dioxide.

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Izvod

KOMPOZITI GRAFENA SA HIDROGELOM

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Kompoziti su višefazni materijali koji se sastoje od dva ili više različitih materijala, različitih svojstava koji su čvrsto vezani jedan za drugi na površini. Kao novi nanomaterijali, grafen i grafen oksid su posebno zanimljivi zbog svoje sposobnosti da formiraju kompozite i nanokompozite sa hidrogelovima. Hidrogelovi su materijali koji imaju trodimenzionalnu strukturu, sposobni da apsorbuju veliku količinu okolne tečnosti bez rastvaranja. Hidrogelovi osetljivi na spoljne stimulanse mogu da promene fizička svojstva kao odgovor na promene nekih faktora spoljne sredine. Hidrogelovi na bazi monomera kao što su *N,N*-dietilakrilamid i *N*-(2-hidroksietil) akrilamid imaju veliki naučni i tehnološki značaj. Našli su primenu u farmaceutskoj, kozmetičkoj, prehrambenoj industriji, industriji boja i lakova, agroindustriji i tekstilnoj industriji. Prethodna istraživanja su dokazala da grafen značajno poboljšava električna, mehanička i termička svojstva hidrogelova. Kompoziti hidrogelova sa grafenom imaju poroznu strukturu. Rad predstavlja literaturni pregled metoda za sintezu i karakterizaciju sintetisanih hidrogelova i kompozita grafena i grafen oksida sa hidrogelom.

(REVIJSKI RAD)

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Ključne reči: kompozit, grafen, hidrogel, sinteza