Hydrophobic Polymer/Graphene and Derivatives Based Nanocomposites: A Systematic Rieview

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Graphene presents exceptional properties. When this nanomaterial is present in nanocomposites, even at low concentrations, their properties are drastically changed and can be tuned according to the desired final nanocomposite characteristics. Graphene-based materials, such as graphene oxide (GO) and reduced GO, can be functionalized with different chemical species, enhancing their versatility. Furthermore, these materials can provide hydrophobic properties for nanocomposites, being useful for applications in anticorrosive coatings, membranes, and packaging. This review analyzed different methodologies/functionalizations reported in the literature to obtain graphene-based nanocomposites with hydrophobic properties.

Keywords: Graphene. Hydrophobic. Nanocomposite.

Introduction

Graphene is a lamellar (2D) nanomaterial with outstanding mechanical, chemical, electrical, and thermal properties. Graphene's structure is based on a single-atom-thick sheet of carbon atoms bonded by sp2-hybridized bonds and arranged in a hexagonal honeycomb lattice. The exceptional mechanical properties of graphene are attributed to the C-C bonds, the most robust connection found in nature [1]. Graphene oxide (GO) is a derivative material from graphene, generally obtained by chemical exfoliation of graphene nanosheets. Unlike graphene, GO presents abundant functional groups bonded to the central carbon sheet, including hydroxyl, epoxide, and carboxylic groups [2].

Consequently, while graphene is considered a hydrophobic material, graphene oxide is hydrophilic, and this property can be tailored depending on the application demand. Functionalization of the GO with different species can produce an extensive range of materials for the most diverse applications. To cite a few examples, graphene and its derivatives can be used on electronics, sensors, batteries, screens, textiles, coatings, packaging, and biomaterials [1,2].

The hydrophobicity effect of graphene and its derivatives is significant for some applications, such as coatings and packaging. A surface can be considered: I. Hydrophilic if the contact angle (q) between the surface and a water droplet on this surface is $10° \leq \theta < 90°$; II. Hydrophobic if $90° \leq \theta < 150°$; III. Super hydrophilic, if $\theta < 10°$; and IV. Superhydrophobic if $\theta \geq 150°$ [1,3].

The superhydrophobic effect results from combining chemical water-repellent species and hierarchical rugosity on the surface. A hydrophobic surface can become superhydrophobic if rugosity is produced on the surface. A natural example of this effect is in the lotus flower, whose leaves are repellent to water drops, which roll over the surface with a contact angle higher than 150°. The leaves present a micrometric rugosity and a nanometric film of wax, which act synergistically to reduce the surface's wettability (Figure 1a) [3].This effect is a consequence of the low energy of the wax on the surface, together with the entrapment of air pockets between the water and the surface due to recesses and projections (micro-structured texture) of the surface [2,3]. For example, biomimetic strategies are studied to achieve this superhydrophobic effect for self-cleaning surfaces (Figure 1b) and anticorrosive coatings. The addition of graphene nanoparticles as fillers in nanocomposites can contribute to the

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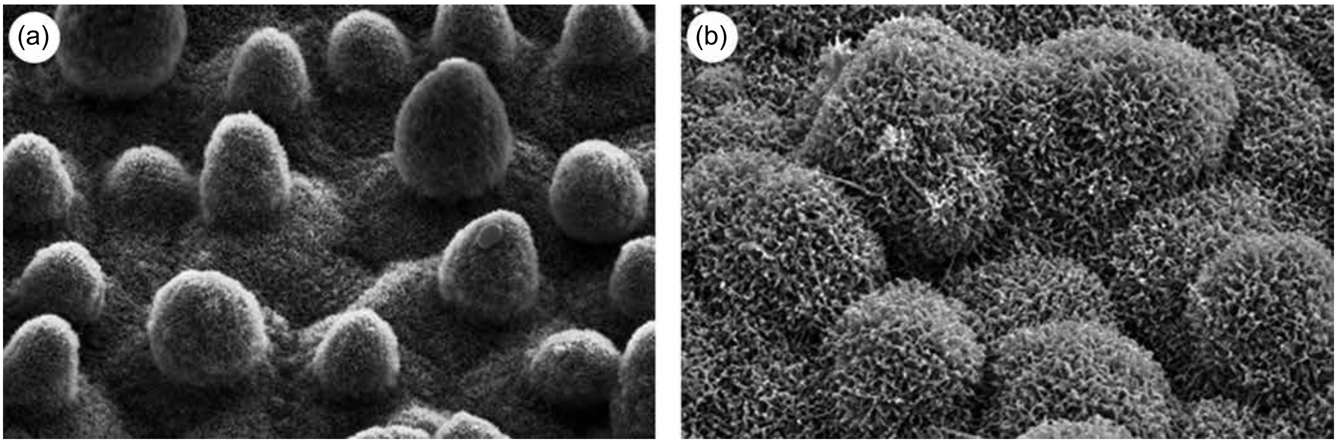
Figure 1. SEM images of the (a) biological model of a lotus (*Nelumbo*) surface and (b) biomimetic copy of an electrochemically hierarchically structured copper foil in the same magnification.



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two factors for the superhydrophobicity effect: The intrinsic hydrophobicity of graphene sheets as well as the addition of irregular rugosity on surfaces due to the presence of the nanoparticles [1].

The exceptional properties of graphene have attracted many researchers and the interest of a wide range of industries. This study's main objective was to develop a systematic review to understand the use of graphene or its derivatives as a hydrophobic filler on nanocomposites, selecting reports from 2017 to 2023. We focused on studies demonstrating the transition of nanocomposite surfaces from hydrophilic to hydrophobic after the addition of graphene and on the graphene or graphene oxide functionalization to achieve more hydrophobic properties.

Materials and Methods

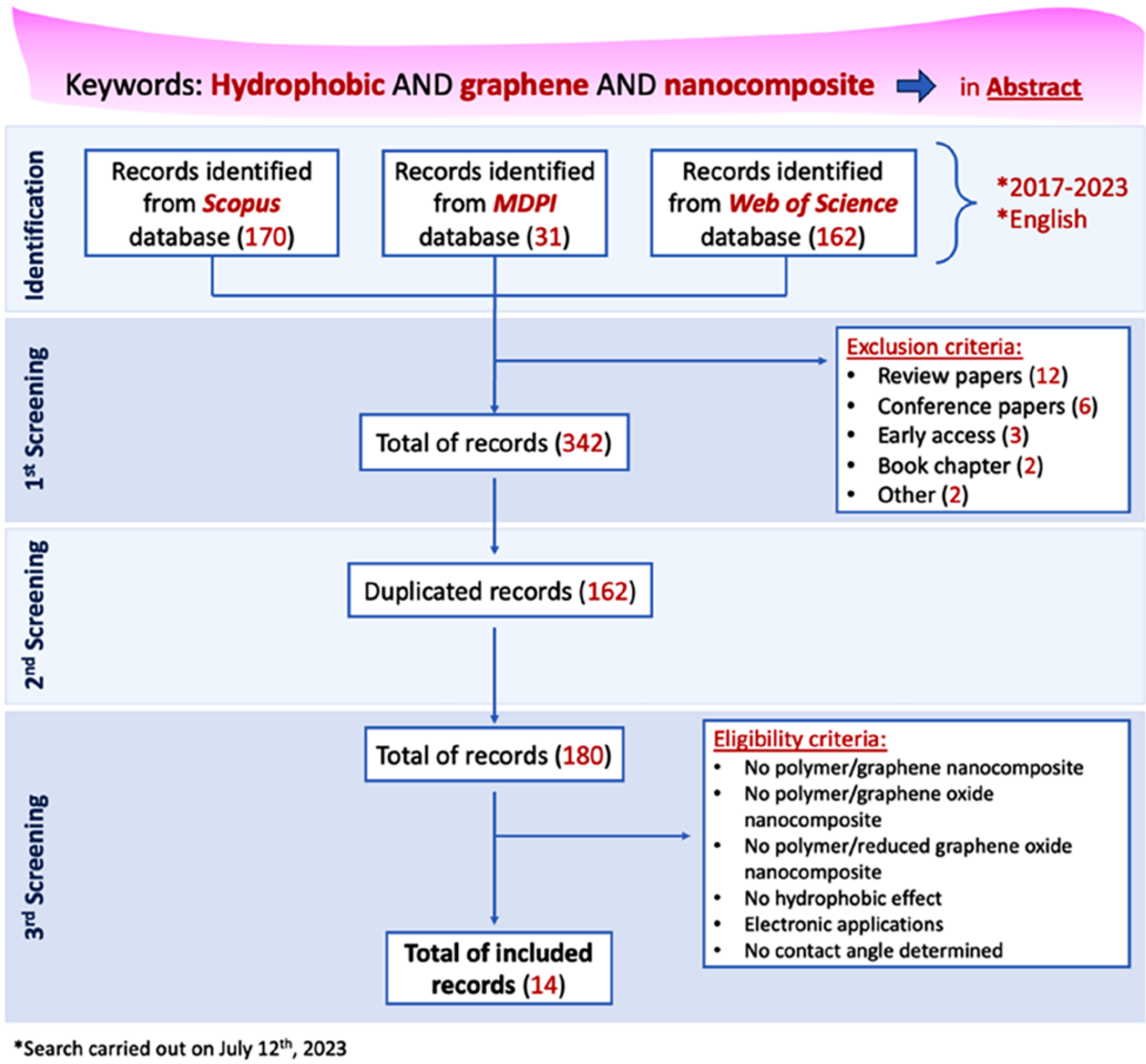
This systematic review followed the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) protocol. Three different literature databases were used to search the papers: Scopus (www.scopus.com, Accessed on: July 12th, 2023), Web of Science (www.webofknowledge.com, Accessed on: July 12th, 2023), and MDPI (www.mdpi.com, Accessed on: July 12th, 2023). The keywords and Boolean operators used for the search were "hydrophobic," AND "graphene" AND "nanocomposite". These three cited keywords had to be present in the paper abstract, and the search included only papers in the English language published from 2017 to 2023.

Figure 2 shows the papers' search and selection process flowchart based on PRISMA requirements. The search in the Scopus, MDPI, and Web of Science databases resulted in 342 papers, including all research articles and excluding review papers (12), conference papers (6), early access articles (3), book chapters (2), and others (2). The next step was to exclude the duplicated papers from the three used databases, leaving 180 documents. At the 3rd screening, due to a large number of studies in various fields, we considered and maintained only the papers concerning polymer/graphene (or derivatives) nanocomposites, related to hydrophobic films or membranes production, presenting oil or water "contact angle" essays, and excluding electronic applications. Finally, 14 papers were considered relevant to be presented in this review.

Data Collection Outcomes

Table 1 summarizes all the papers selected using the systematic review protocol (PRISMA) (Figure 2).

Figure 2. Systematic review flowchart, following PRISMA protocol.



Zhou and collaborators (2017) [5] obtained a superhydrophobic property by coating a PET film with GO functionalized with octadecyl amine (GO-ODA). While the PET film coated with only GO coating (2 mg/mL) presented a water contact angle (WCA) of 21° (hydrophilic due to the hydroxyl and carboxyl groups of GO), the GO-ODA coating (2 mg/mL) exhibited a very high superhydrophobic effect, presenting WCA of 164°, attributed to the long carbonic chains of ODA. Similarly, Xu and colleagues (2019) [16] used octadecylamine (ODA) functionalized GO (GO-ODA) as filler in regenerated cellulose films to enhance the water vapor barrier performance of the nanocomposite films. Pure GO presented WCA=38°, while GO-ODA increased the contact angle to 126° due to the hydrophobic carbonic chains of ODA, which contributes to the water repellence.

Yadav and colleagues (2023) [12] produced hydrophobic polyurethane foams with different GO concentrations (0%, 1%, 2%, 3%, 4%, and 5%) for application as oil sorbent apparatus for water decontamination and for recovering oil and organic solvents from polluted natural waters.

Table 1. The polymeric matrix, graphene type, functionalization species, nanoparticles (NP) concentration, and water contact angle of the surfaces with and without graphene or functionalized graphene of the selected papers.

Reference	Polymeric Matrix	Graphene Type	Functionalization Species	Water Contact Angle (Without NP)	Water Contact Angle (With NP)	NP Conc. (wt.%)
Bera and colleagues (2020) [4]	Thermoplastic Polyurethane (TPU)	GO	p-phenylenediamine (GO-PPD); hexamethylenediamine (GO-HMD); ammonia (GO-NH_3)	87° (TPU); 84°(TPU/GO)	96,7° (TPU/GO-PPD); 105,3° (TPU/GO-HMD); 90,7° (TPU/GO-NH_3)	0.1
Zhou and colleagues (2017) [5]	Polylactide (PLA)	GO	Octadecylamine (GO-ODA)	21° (PET/GO)	164° (PET/GO-ODA)	0.2
Ravi and colleagues (2021) [6]	Polyvinylidene difluoride (PVDF)	GO	Perfluorodecyltriethoxysilane (PFDTES)	85° (PVDF)	100° (PVDF/1%GO-PFDTES) 110° (PVDF/2%GO-PFDTES)	1.0 2.0
Paseta and colleagues (2020) [7]	Polyamide (PA)	rGO	Octadecylamine (ODA)	70° (PA)	81° (PA-rGO-ODA-0.03) 84° (PA-rGO-ODA-0.06)	0.03 0.06
Zhang and colleagues (2023) [8]	Epoxy (EP)	rGO	Polyaniline (PANI) + $CePO_4$	51° (Epoxy)	92° (EP-rGO-PANI/$CePO_4$)	1.0
Wang & Lin (2021) [9]	Epoxy (EP)	G	--	52° (Epoxy)*	110° (EP-Graphene + Silica)*	1.0
Xavier & Vinodhini (2022) [10]	Epoxy (EP)	GO	Nano Zr_2C + 3-aminopropyl tris[2-(2-methoxy ethoxy) ethoxy] silane (APTMEES),	68°(Epoxy)	161° (EP-GO/APTMEES-Zr_2C)	2.0
Ramirez-Soria and colleagues (2021) [11]	Epoxy (EP)	GO	NH_2 and NH_3+ (BFGO)	62° (Epoxy)	105° (EP-BFGO)	0.5
Yadav and colleagues (2023) [12]	Polyurethane (PU) foam	GO	--	124° (PU foam)	135° (PU-4-GO)	4.0
Ly and colleagues (2021) [13]	Poly(acrylic acid) (PAA) + Poly(ethylene imine) (PEI) + Poly(sodium 4-styrene sulfonate) (PSS) + Poly(allylamine hydrochloride) (PAH)	rGO	Poly(sodium 4-styrene sulfonate) (GPSS) and Poly(allylamine hydrochloride) (GPAH)	130° $(PEI/PAA)_{60}$ Layer-by-Layer film	136° $(GPAH\text{-}PEI/GPSS\text{-}PAA)_{60}$ Layer-by-Layer film	--
Ramirez-Soria and colleagues (2022) [14]	Epoxy (EP)	GO, rGO	Propyl-GO and Propyl-rGO	62° (Epoxy)	95° (EP/propyl-GO) 100° (EP/propyl-rGO)	0.5
Rajitha & Mohana (2020) [15]	Epoxy (EP)	GO	2-Aminothiazole (GO-AT) and 2-amino-4-(1-Naphthyl) Thiazole (GO-ANT)	86° (Epoxy)	92° (EP/GO) 95° (EP/GO-AT) 97° (EP/GO-ANT)	0.2
Xu and colleagues (2019) [16]	Regenerated cellulose	GO	Octadecylamine (GO-ODA)	38° (GO)	126° (GO-ODA)	0.5 1.0 2.0 5.0
Abakah and colleagues (2021) [17]	Epoxy (EP)	Commercial G (X50, M15,C750)	--	64° (Epoxy)	72° (EP/X50) 81° (EP/M15) 102° (EP/C750)	1.0

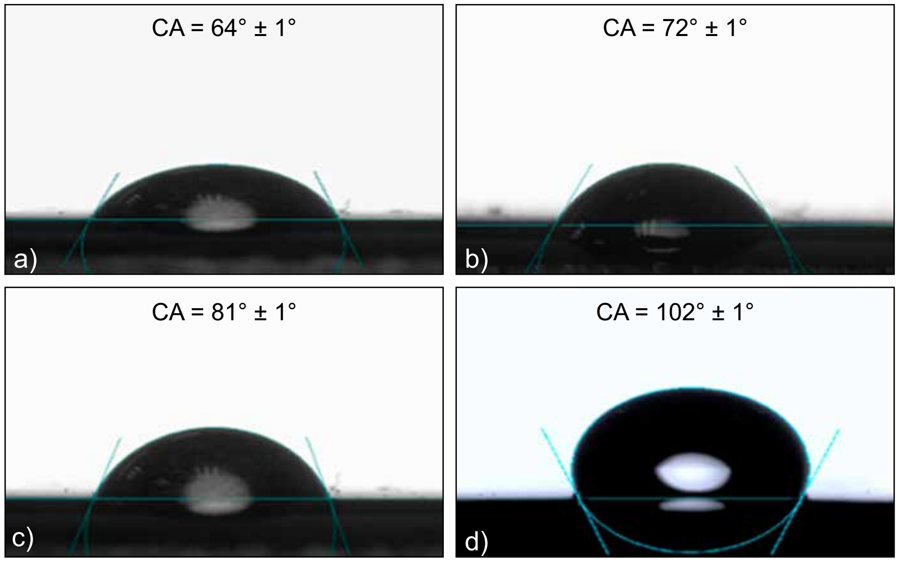
*Data obtained after abrasion test.

The authors evidenced the excellent oil absorption capacity of the foams, which is super-lipophilic and, therefore, highly hydrophobic. The authors reported that the PU foam without GO exhibited a water contact angle (WCA) of 124°, and even after the 500th reuse cycle, the WCA was maintained hydrophobic, with WCA=105°. This effect can be due to the hydrophobic polymeric chains of PU and the high rugous foam surface. Furthermore, Yadav and coauthors found that among the concentrations of GO studied, 4 wt.% of GO in the PU foam increased its hydrophobic effect, presenting initial WCA of 135° and 111° after the 500th reuse cycle. Ly and colleagues (2021) [13] reported the development of a hydrophobic film composed of multilayers of polyelectrolytes with opposite charges using the Layer-by-Layer assembly technique. The authors used the positively charged polyelectrolytes Poly(ethylene imine) (PEI) and Poly(allylamine hydrochloride) (PAH). In contrast, Poly(acrylic acid) (PAA) and Poly(sodium 4-styrene sulfonate) (PSS) were used as the negatively charged polyelectrolytes. The hydrophobic film was produced by depositing alternatively positively (PEI+PAH+rGO mixture) and negatively (PAA+PSS+rGO mixture) charged nanocomposites on a glass plate surface, repeated 60 times. The authors noted only a slight increase in the WCA after adding the rGO nanoparticles, from 130° for the $(PEI/PAA)_{60}$ film (without rGO) to WCA=136° for the $(GPAH\text{-}PEI/GPSS\text{-}PAA)_{60}$ film (with rGO). AFM analyses revealed a rougher surface for the (GPAH-PEI/GPSS-PAA)60 nanocomposite than for the (PEI/PAA)60 film due to the presence of the nanoparticles, creating a hierarchical structure that increases the surface hydrophobicity. In 2022, Ramirez-Soria and collaborators [14] demonstrated a hydrophilic-hydrophobic transition of epoxy coating by adding only 0.5 wt.% of propyl-functionalized GO or rGO. While the pure epoxy coating presented a hydrophilic WCA of 62°, the epoxy coating loaded with propyl-GO increased the water repellence, exhibiting WCA=94°. Since propyl-rGO presents a smaller number of hydrophilic groups than propyl-GO, adding propyl-rGO to the epoxy coating increased the hydrophobic behavior to WCA=100°. Abakah and colleagues (2021) [17] tested the effect of three different commercial graphene types (X50, M15, C750) on epoxy nanocomposite properties. C750 graphene presents a medium diameter of up to 2 mm, M15 has a medium diameter of up to 15 mm, and X50 exhibits nanoparticles with a diameter of about 150 mm. The WCA of the neat epoxy coating was 64°, demonstrating a hydrophilic nature. The epoxy nanocomposite with 1 wt.% of X50 showed a WCA of 72°, while the nanocomposite with the graphene M15 presented WCA=81°, and the EP/C750 nanocomposite presented WCA=102°, demonstrating a hydrophobic behavior (Figure 3). Considering that the three graphene types do not have hydrophilic functional groups, the differences in the wettability properties can be related to the diameter of the graphene nanoparticles and their respective surface area, consequently producing rough surfaces on the nanocomposites. The C750 graphene nanoparticles, which have the most minor diameter among the three types of graphene used (up to 2 mm), probably produced the roughest surface with a hierarchical structure. Furthermore, the nanocomposite EP/C750 presented the best corrosion protection performance.

Conclusion and Future Perspectives

Graphene presents fascinating properties for strategic and commercial applications. Many scientific researchers and industrial interests involving graphene synthesis and functionalization to diverse applications demonstrate how this 2D nanomaterial has excellent potential to be present in the most diverse recent technologies. Hydrophobicity is only one of the properties that graphene and derivatives can provide to graphene-based nanocomposites, and superhydrophobicity can be achieved by using functionalization methods and producing hierarchical structured surfaces with at least two different scale levels. As described in this review, many studies report the hydrophobic effect of graphene-based materials

Figure 3. Surface contact angle of (a) pure epoxy (EP), (b) EP/X50, (c) EP/M15, and (d) EP/C750 coatings.



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in nanocomposites, but the superhydrophobicity effect is still scarce in the literature. Exploring new chemical species and functionalization methods and producing biomimetic surfaces can be the next step to achieving more water-repellent and self-cleaning surfaces.

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