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REVIEW ARTICLE

A systematic review of enhanced polyurethane foam composites modified with graphene for automotive industry

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Abstract
Polyurethane foams are obtained during the reaction of compounds with hydroxyl groups and compounds containing isocyanate groups and are widely used in the packaging, construction, transportation and electrical energy industries. To bring benefits to its properties, several types of reinforcement are added to polyurethane foams, such as improvements in the thermal, mechanical, fire resistance and thermal insulation of the PUF. Thus, this article presents a systematic review of graphene-modified polyurethane foam composites for acoustic and structural applications with a focus on the last five years. The investigation followed the PRISMA protocol which provides a meticulous summary of all available research in response to a research question. After the inclusion/exclusion of the steps, thirty one studies were included in the review. The results were presented with a focus on PU foam fabrication techniques, polyol types, carbon structured reinforcements and techniques for fabrication of filled graphene PUFs and sound properties. In short, this methodology helped to identify the main knowledge gaps in this area.

Keywords Systematic review · Composites · Polyurethane foam · Graphene · Acoustical properties

1 Introduction and global scenario

Polyurethane foams (PUF) were firstly synthesized in the 1950s and have been used in many areas due to their versatility. Rigid polyurethane foams (RPUF) play an essential role in many industries, such as construction, refrigeration, piping and automotive. For instance, in automotive industry foams are used in parts like the seats, bumpers, the inner section of the "headliner" roof, car body, spoilers and all doors and windows. In this regard, mechanical and acoustical properties play a major role for automotive and mobility sector, and the understanding of these properties mechanism is fundamental for the manufacturing of cheap and high performance foams [1–3]. Different types of PU foams, rigid or flexible, may be obtained, depending on the raw materials (polyol and isocyanate) and additives employed in the PUF synthesis [4]. The combination of additives may produce foams with high, medium or low density and high or low flexibility.

Briefly, surfactants are employed with the purpose of regulating the polymer apparent viscosity, aiming to produce foams with a more stable cell structure and low friability. Surfactants are generally oils, with inert characteristics and do not participate in the polymerization or kinetic reaction. Some silicone oils are commonly used for this purpose, some examples include poly (dimethylsiloxanes) and poly (phenylmethylsiloxanes), important in flexible and semi-flexible foam systems.

Catalysts are used for decreasing the energy required to start the reaction between hydroxyl and isocyanate groups, to form the urethane bonds, and then, reduce the time for the PU synthesis. Tin compounds (such as tin octoate and dibutyl tin dilaurate) are very useful in promoting the gelation reaction, but they are very sensitive with respect to hydrolysis stability. In this sense, amino-based reactants may be employed. Some examples include triethylenediamine and 4-dimethylaminopyridine (DABCO).

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Usually, chain extenders (molecules with low molecular weight and functional groups) are employed for the increase on the foams' strength and stiffness. Chain extenders are usually employed aiming to increase the polyol's chain extension and the degree of polymerization of the formed PU. It promotes a high number of branches capable of forming bonds with NCO groups belonging to isocyanate. Some chemicals used for this purpose include glycols (e.g., polyglycols, glycerol and butanediol).

Different blowing agents may also be employed for PUF expansion. Usually, water is the most blowing agent employed for PUF expansion. However, if a high control of cell's foams morphology is required, trichlorofluoromethane (137.4 g/mol) and n-pentane (72.2 g/mol) would be used, in addition to the polymerization conditions [4, 5].

The most common feedstock for PUF synthesis come from petrochemicals, such as polyesters or polyether polyols and isocyanates, such as methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI). On the other hand, PUF market have been increased in the last few decades, due its versatility and easiness to obtain different properties, depending the aforementioned chemicals employed for its synthesis. In this regard, aiming to obtain a higher environmental appeal, bio-based polyols have been used for PUF synthesis. Castor oil, palm oil, soy bean, among other fat oils are developed day by day aiming to replace conventional petrochemical reactants [6, 7].

Despite the aforementioned advantages in using oils from renewable resources, these feedstocks present some drawbacks. It is well known that bio-based foams present low mechanical response, thermal stability and sometimes friable characteristics. Aiming to by-pass these disadvantages, fillers may be employed, regardless the foam is flexible or rigid, aiming to produce a material with greater performance [8–11]. Bio-fillers (fillers from natural resources, without major chemical modification and/or treatment) may also be used aiming to manufacture a PUF with high performance and environmentally friendly characteristics. In addition to being abundant and renewable resources, bio-fillers are easily chemically modified, resulting in foams with enhanced mechanical properties, relatively low cost and greater thermal stability [9]. Furthermore, structural modification of polyols is usually carried out by adding flame retardants, which cause deterioration of mechanical and/or thermal response. Then, to pay-pass this concern, the addition of fillers is usually required [7].

For instance, Zhou et al. [9] produced semi-rigid PUF, using palm oil as polyol and cellulose nanocrystals (CNC) as reinforcement for the bio-polyol (BPU). The foams' properties were compared with those produced using a petrochemical polyol (PPU). According the results, those PPU presented thicker cell walls and larger cell struts than those of the BPU foam. The compressive strength (10% deformation) of BPU foam is lower than that of PPU foam, 54 and 125 kPa, respectively. On the other hand, with the addition of 4 phr of CNC, there is a twofold increase in the compressive strength of the BPU4 foam (117 kPa).

Another vegetable oil widely studied for the production of PUF is castor oil, in which we find ricinoleic acid as the main fatty acid. This acid naturally has an enough content of hydroxyl groups, functional groups important for the synthesis of PUF. The adequate amount of these functional groups means that there is no need for chemical modification and it can be used directly as a polyol for the PUF's synthesis. Furthermore, the uniform distribution of these groups in the castor oil chain enables the synthesis of PUs with a more uniform cross-linked structure, high mechanical performance and thermal stability. Also, the use of this oil becomes interesting for the production of PUF on an industrial scale because it is a non-food seed vegetable oil, not competing with food, and can be obtained at a lower cost [4, 9, 12].

To solve these challenging issues, many efforts have been paid to develop high performance PUF. The incorporation of fillers in polymeric matrices improves their mechanical properties. Several studies bring the incorporation of different fillers in PUF, such as micro-fibrillated cellulose [8], rice husk ash [11], cellulose nanocrystals [9], silica nanoparticles [13], kaolin clay [14], in addition to carbon structures such as graphene oxide [14–16]. The addition of graphene oxide gives PUFs greater thermal and mechanical response, electrical conductivity and a high surface area, when compared to carbon nanotubes, for example [17]. These foams have characteristics such as flexibility, lightness, low cost and can be used in different applications, one of which is acoustic insulation [18].

Sound absorption is influenced by several factors, in foams, morphology (associated with the cell wall structure) and pore characteristics (size, quantity, interconnectivity, tortuosity) are the most important. The airflow resistivity provided by the cell walls in foams with small interconnected pore structures provides a better sound absorption coefficient. Also, porosity, associated with low density, offers less resistance to sound waves dissipation, resulting in a low sound absorption coefficient. With the incorporation of GO, there is an increase in the compression modulus, and thus the cells are more likely to undergo cell stretching, bending and buckling without deformation [19].

Based on this, the objective of the present paper is to discuss the recent progress of the addition of graphene as reinforcement in polyurethane foams. The type of composite (if only graphene or hybrid composites) studied, as well as the methodology of adding reinforcement into PU foams will be detailed. Besides, the main differences in morphology and its reflection on the mechanical and acoustic response are presented and discussed in detail.

2 Systematic review methodology

The systematic review of recent studies of polyurethane foam reinforced with graphene oxide was carried out based on the methodological guidelines outlined by the Transparent Reporting of Systematic Reviews and Meta-Analysis (P.R.I.S.M.A.). The papers were select using the Scopus (www.scopus.com), Web of Science (www.webofknowledge.com) and Mendeley (www.mendeley.com) online databases. Figure 1 presents the evolution of publications in the three data bases used for this work with the keywords previously listen. It is noteworthy that the total number of papers in 2011 was only 2 and, in 2019, 44, having an increase in 2100%.

The search terms used were *polyurethane* and *graphene* and *foam*, need to be at least on the abstract. The results were limited to English language, only research papers and published within 2017–2022. From the articles listed in the three databases, the titles and abstracts were read independently by two reviewers (Eduardo Kerche and Lídia K. Lazzari) to identify their suitability.

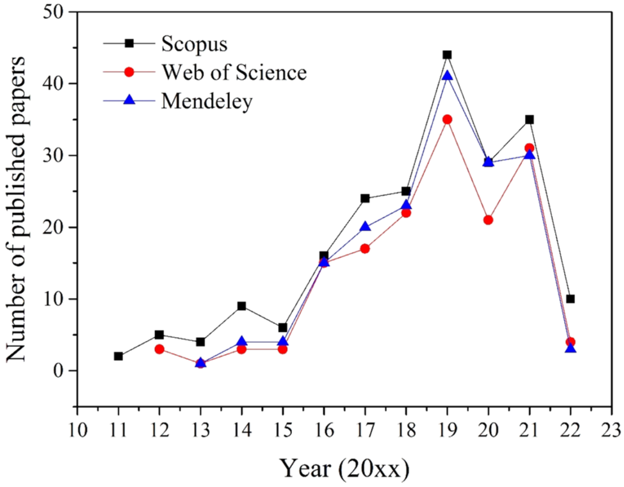


Fig. 1 Evolution of publications about graphene and polyurethane foams

In agreement with both reviewers, some criteria were selected as relevant or irrelevant for the analysis of the papers, they are listed in Table 1. Some analysis and results that were evaluated and compared between the papers are listed in Table 1 as relevant criteria for paper inclusion. Besides, some exclusion criteria are listed since they don't attend to the study scope.

3 Results of data collection

The selection of studies (number of studies and studies included or excluded) is shown in Fig. 2 based on P.R.I.S.M.A. requirements. The search in the Web of Science, Scopus and Mendeley databases resulted in 502 articles, excluding review articles, in languages other than English, conferences, and duplicate articles, leaving 160 documents. Considering the relevant and irrelevant criteria presented in Table 1, at the end of the careful analysis of each of the 160 articles, 31 articles were considered relevant to be included in this study.

3.1 Discussion of results

The papers were further classified based on the polyol type, the reinforcement used, and impregnation process of the reinforcement, and this is shown in Fig. 3.

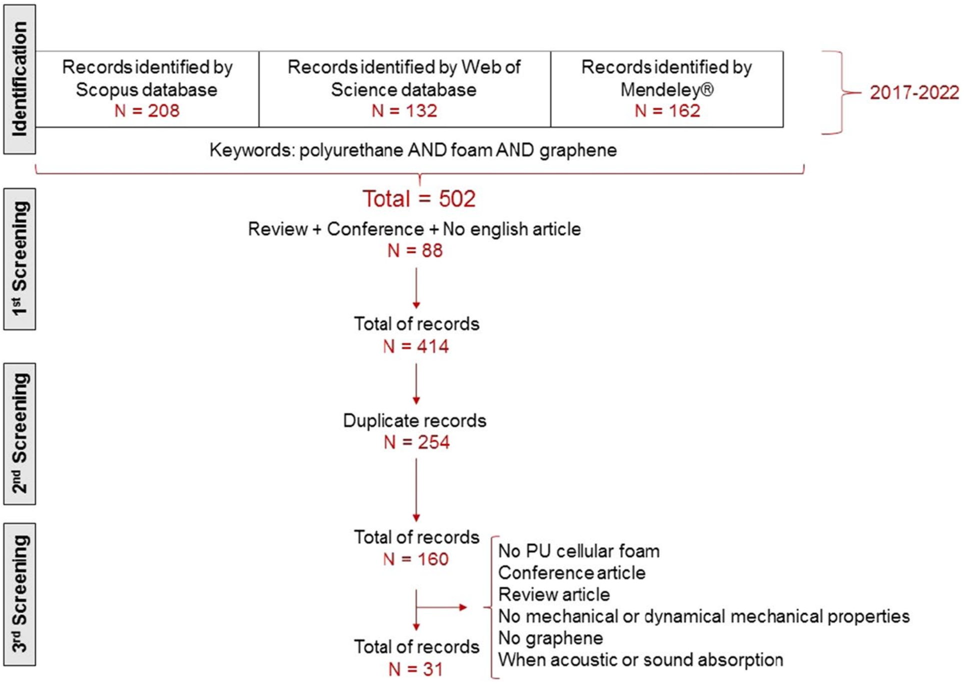
Regarding the type of polyol (Fig. 3a), the vast majority of foams found in this review were produced with commercial non-bio-based polyol (96%). The authors focused on evaluating the effect of reinforcement on foam properties rather than to synthesize the foam.

Regarding the type of reinforcement (Fig. 3b), about 59% of the articles use graphene oxide (GO) as reinforcement for polyurethane foams, graphene nanoplatelets are also widely

Table 1 Relevant/irrelevant criteria for the papers' analysis

Relevant criteria	Irrelevant criteria
Density or cellular structure (SEM images or micro tomography)	Graphene was not the main objective of the study or when only comparisons of the paper's results with other paper from literature that use graphene is made
Flammability	No PU cellular foam
Sound absorption or acoustic properties	PUF for microwave radiation were not considered
Mechanical properties	Sandwich structures were not considered
Different dispersion techniques impact directly on the mechanical response	When acoustic or mechanical response are not the focus of the paper
Hybrid foams (i.e., if there is more than one reinforcement) were considered. However, if graphene filler was not the main focus of the paper, it was not considered	Nano-DMA or papers that do not bring a real contribution about acoustic insulation and the effect on different methodologies and materials on it

Fig. 2 Systematic review flowchart, in accordance with PRISMA protocol



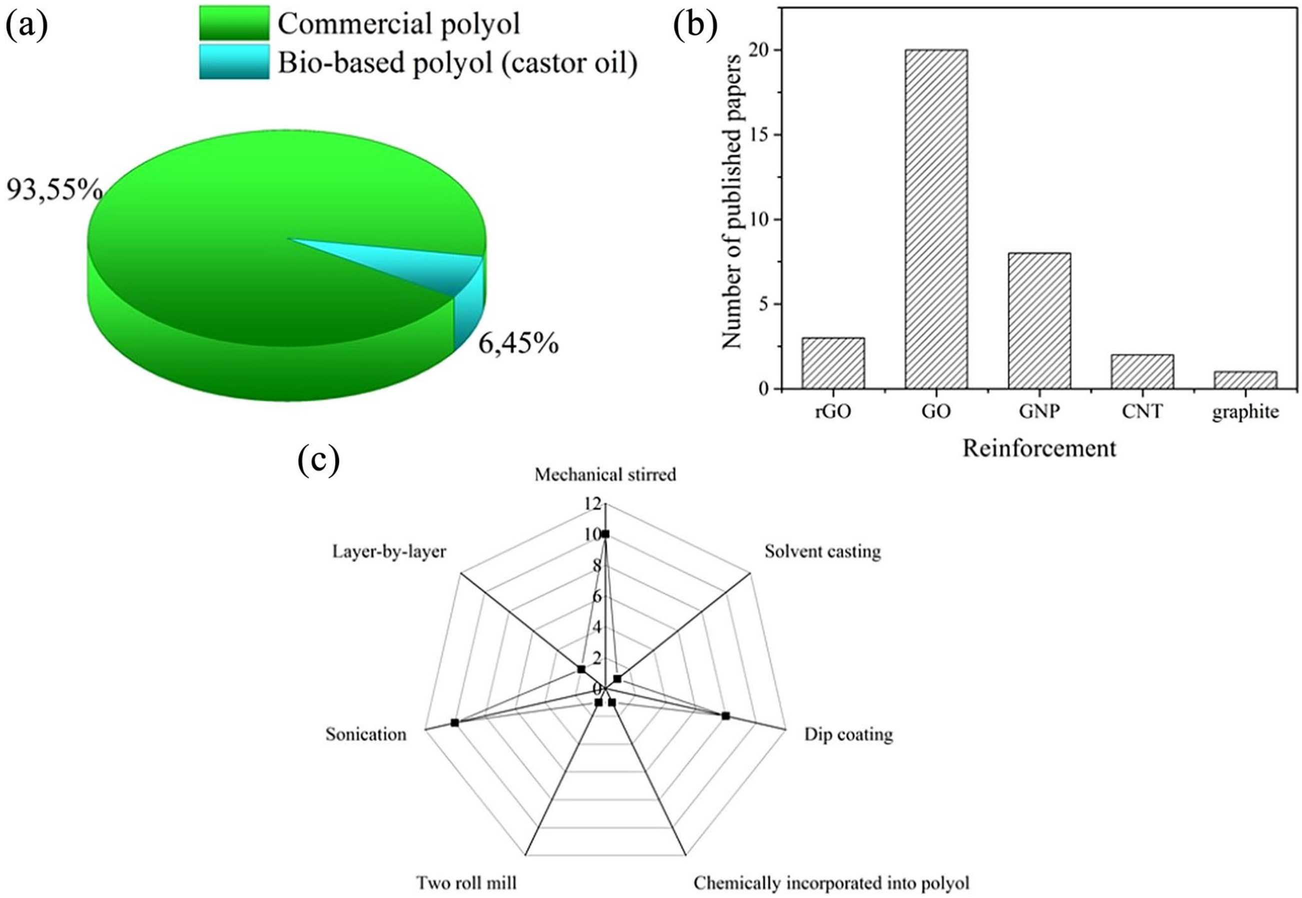


Fig. 3 Polyol type (**a**), type of reinforcement (**b**) and impregnation process (**c**), reported in the papers found in this systematic review

used, about 23% of the articles use this reinforcement, reduced graphene oxide, carbon nanotubes and graphite are also mentioned.

The addition of reinforcements occurs in two ways, the impregnation of the reinforcements in the polyols (67%) or deposition on the foams' cell structure (33%). The impregnation of the reinforcements in the polyol occurs, mostly, by mechanical processes, with the mixing of the reagents by mechanical agitation and two roll mill or sonication of the reinforcement in the polyol solution, or chemical modification of the polyol. The second way is to deposit the reinforcement on the polyurethane foam cell structure through methods such as dip coating, layer-by-layer and solvent casting.

The 31 articles referenced in this review are summarized in Table 2. In addition to the characteristics of the type of polyol, reinforcement and reinforcement impregnation methodology, Table 2 also presents the type of foam produced, the amount of reinforcement used and the main results found by the studies.

3.2 Polyurethane foam manufacturing techniques

Regarding the manufacturing techniques employed to PUF, free rise expansion is by far the most used technique for the fabrication of components, due to its easiness of processing and not the needing for complex apparatus or machinery for the production of components in large scale [35]. However, in current literature, not only simple techniques are employed for the manufacturing of PUF, but the expansion and reaction into closed molds are explored.

Polyurethane foams, expanded into closed molds, present a more regular cellular structure and great cell size distribution and uniformity [8, 45]. Moreover, the density's fitting and adjustment may be due, depending on the application and final product destination. For instance, it is possible to manufacture a foam with high density to be used in structural application with the same formulation as that used in upholstery. Some models, using statistical approaches, may also be employed to predict the final product density and property, in a specific range, this is also an advantage in using a closed mold to manufacture the components using PUF [46].

Many methods have been proposed to create TPU foams, such as in situ polymerization using water as a foaming agent, gas foaming, salt leaching, phase inversion and water vapor induced phase separation. The use of supercritical fluids as blowing agent, and in particular carbon dioxide (sc–CO_2), has become a promising and efficient strategy for the preparation of microcellular polymeric foams [47].

Indeed, differently from a free rise expansion, using blowing agents such as water, chlorofluorocarbons, hydrochlorofluorocarbons and methylene chloride [48] PUF produced by $scCO_2$ present a more controllable and thinner cell structure rather those freely raised PUF. Furthermore, this technology is low cost, used in moderate conditions ($T \approx 30$ °C, $P \approx 7$ MPa), lowered burden, on the environment, and greater safety offered, compared to the aforementioned blowing agents. Finally, this technology also possesses the great advantage of being easily scaled-up to industrial level [42].

3.3 Polyol types

Polyols and poly isocyanates are the main sources of raw materials to produce PUF. There are several types of raw materials for the PUF production, however, those from petrochemical industry are the most diffused in industry, due to their well-known better performance, compared to bio-based ones, such as higher mechanical and thermal properties as well as fire resistance. However, with the use of PUF growth day by day, the generation of waste is an alarming concern for environmental protection, so proposals for eco-friendly PUF arise all the time [7].

One way to relieve this problem is the use of raw materials, derived from renewable sources, such as vegetable oils [8–11]. In addition to being more abundant, they are easily chemically modified, resulting in excellent properties and relatively low cost of final products [9]. This chemical modification of polyols directly affects the structural and morphological characteristics of the final PUF. These differences are usually carried out by the incorporation of additives, such as fillers, flame retardants, open cell agents and so on. However, some of these modifications bring a detrimental effect on mechanical and dynamical mechanical properties as well as in the cell structure distribution and growth [7].

Castor oil (CO) is one example of bio-based polyol. CO is composed primarily of ricinoleic acid, a fatty acid that presents, naturally, hydroxyl groups, a functional group important for the synthesis of polyurethane, which react with the isocyanate to form a urethane bond, by block polymerization. The adequate amount of these functional groups means that there is no need for chemical modification, and it can be used directly as polyols, for the PUF synthesis. Besides, the uniform distribution of these groups in the castor oil chain enables the synthesis of PUs with a more uniform cross-linked structure, which enables high mechanical performance and thermal stability, desired properties for RPUF. Furthermore, the use of this oil becomes interesting to produce bio-based PUF on an industrial scale, because it is a non-food seed oil, not competing with food, and can be obtained at a lower cost, contrasting with other oils, such as soybean [4, 12, 49].

Table 2 Synthesis of articles referenced in this review

References	Graphene type	Amount	Polyol/isocyanate type	Impregnation technique	Foam type	Mechanical/dynamical mechanical or acoustical property and density or specific mechanical property
[20]	Hybrid rGO modified with copper salt	3 wt.% of hybrid filler, in relation to the polyol	Polyether polyol/TDI	Mechanical staring	FPUF, open cell, low density (≈28.5 kg/m^3)	Increases in TS from 60 kPa (neat FPUF) to 100 kPa and increase from 31.45 to 88.07 kPa in CS, depending the copper oxide used. No significant differences in density (≈29.8 kg/m^3). Also increasing the fire resistance
[21]	GNP	0.1, 0.25 and 0.5 wt.% of NPG in relation to the RPUF	polyether, polyester-ether and polyester	Sonication of NPG into the polyol with additives (1 h)	Closed cell, RPUF, medium density (≈60 kg/m^3)	10.7% and 66.5% increases on CS and CM, respectively, when 0.25 wt.% of NPG was used. Decrease on density from 64.3 (neat RPUF) to 56.75 kg/m^3 (0.5 wt.% of NPG in relation to RPUF)
[22]	GNP	1 or 2 wt.% in relation to the MDI	Polyol polyether/MDI	Sonication (10 min.) of GNP into the MDI	Flexible, open cell	Neat RPUF with TS and TM of 238 and 94 MPa and with 2wt.% of GNP filler. Densities of 586.6 kg.m^3 for neat foam and 388 for those PUF with 1 wt.% of GNP. T_g of –42 for neat foam and –40 °C for those with 2wt.% of GNP
[23]	GO/Fe$_3$O$_4$ nanohybrid	1 wt.% in relation to RPUF	Polycarbonate diol/TDI	Sonication of the hybrid filler into DMF and posterior dispersion into TDI	Rigid, closed cell	12.5% increase in CS at 10% strain and the CM by 7.0%. Increase in density from 480 to 536.7 kg/m^3 for neat PUF and the composite, respectively. T_g from 22.8 to 27.3, for neat and composite PUF, respectively

Table 2 (continued)

References	Graphene type	Amount	Polyol/isocyanate type	Impregnation technique	Foam type	Mechanical/dynamical mechanical or acoustical property and density or specific mechanical property
[24]	GO	0.033 wt.% in relation to RPUF	Poly (propylene oxide) polyol/pMDI	In-situ synthesis of polyol containing GO	Rigid, closed cell	The study is a sequence from a previous [8]. The influence of catalyst, surfactant and isocyanate index were studied. The composites with the additive's' optimized content presented 4% in density reduction, increase in 60% and 40% in the compressive modulus and collapse stress, respectively
[16]	GO	0.3 g/L of GO in water solution	Commercial/not specified	Coated with graphene by dipping several times in a low-concentration aqueous graphene oxide (GO)	Semi-open cell, flexible, low density	Improvement on the sound absorption coefficient on the frequency range of 50 Hz to 6, 4 kHz. Improvements on the cyclic compression characteristics. CS from 1.9 (neat PUF) to 18.72 and 8.02 kPa, depending the PUF composite manufacturing
[25]	GO	0.5 wt.%	Castor oil functionalized with phenylphosphonic acid/	Mechanical staring of GO. Comparison of GO and expandable graphite	RPUF with castor oil or modified castor oil	Equal results for CS for those with GO or graphite. Reduction of CS when these fillers are employed from 146 to 109 kPa, compared with the PUF manufactured with the modified bio-oil. Reduction of density from 31.8 to 30.4 kg/m^3, for neat foam or GO foams
[26]	GO	0.25 and 5.0 wt.% in relation to coating	Commercial polyester foam	GO (sonicated) into a siliconeresin (SiR) solution	FPUF	CS from 1.93 to 2.24 MPa comparing the coated foam with the coated foam with GO. Improvements of flame retardancy

Table 2 (continued)

References	Graphene type	Amount	Polyol/isocyanate type	Impregnation technique	Foam type	Mechanical/dynamical mechanical or acoustical property and density or specific mechanical property
[27]	GNP and MWCNT	.25, 0.50 and 0.75wt.% of hybrid nanofiller	Commercial, not specified	ultrasonic bath and mechanical stirring	Closed cell, RPUF, density of 40.51 kg/m^3	Improvement of ≈19, 21 and 24% in TS, using 0.25wt.% of MWCTN and 0.25 and 0.5wt.% of GNP. 0.25wt.% of GNP increased the impact strength of PU about 13.4% and 5.4%, respectively. No experimental density information
[28]	GO	Aqueous solution of GO (0.5 mg mL^{-1}) mechanically stirred	Commercial/not specified	PUF is dip-coated several times in a solution of GO	Commercial FPUF open cell, low density foam	Increase in density from 17 to 49 and 52 kg. m^{-3}, depending the manufacturing process, but no increases when only GO is used. Increase in damping ratio from 2.34 to 4.39, depending the manufacturing. Increase in noise reduction coefficient from 0.158 to 0.448. Absorption of 98.4% of sound depending the manufacturing condition
[15]	Isocyanate modified GO	0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 wt.% in relation to	Polyether and polyester polyol/PAPI	Ultrasonic dispersion of modified GO into PAPI	RPUF, closed cell	Dramatical increase on E’, T_g increase from 117 to 138 °C, for those RPUF with 1.5wt.% of modified GO. Density from 44 (neat) to 47 (RPUF with 1.5wt.%) kg/m^3, With the increase in filler content, both the compressive strength and modulus first increased and then decreased, with the maximum values obtained at 1.5wt.%

Table 2 (continued)

References	Graphene type	Amount	Polyol/isocyanate type	Impregnation technique	Foam type	Mechanical/dynamical mechanical or acoustical property and density or specific mechanical property
[29]	GNPs	0.05, 0.1, 0.2, 0.3 and 0.4 phr	Polyether polyol/MDI	High speed mechanical mixing of GNP with MDI	FPUF, open cell, low density PUF (≈19 kg/m^3)	Increase of sound absorption coefficient from 0.44 (neat) to 0.52 (0.2 phr of GNP). No significant differences in density
[18]	Hybrid CNTs, GO and silver nano particles	≈7 mg. ml^{-1} of GO into a solution	Polyether polyol/MDI	Solvent casting method	FPUF	Hybrid fillers increased TS by 323%, compared with neat. Density not reported
[30]	GO	0.5 mg ml^{-1} of GO into water and sonified	Commercial FPUF/not specified	GO dispersed into water, sonicated and the PUF was squeezing and vacuum degassing and dried	Commercial FPUF/not specified	Storage modulus from 4.82 (neat FPUF) to 9.15 MPa T_g from 51.2 to 41.2 °C. Density not evaluated
[31]	GO	1–4 mg/mL of into MDF	Commercial TPU foam	Coating of GO on the PUF surface	Thermoplastic PUF	Increase from 6.47 to 68.24 N of CS and from 198 to 2041 kPa (PU with GO and PU with modified GO, respectively). Increase in density from 30 to 750 mg/cm^3, for PU with GO and PU with modified GO, respectively
[1]	Hybrid rGO and cellulose filaments	0.025 and 0.05 wt.% of rGO	Polyol polyether/MDI	Mechanical staring	FPUF, medium density, open cell	Decrease in density from 56.4 (neat) to 43.6 (0.025 of rGO) kg/m^3. Increases from 25 to 45 kPa in CM and from 125 to 150 in TM
[32]	GO	0.5–1 wt.%	Polycarbonate diol/TDI	Sonication of GO into DMF and PUF pre polymer	polyurethane-imide foams, high density (≈490 for neat PUF), closed cell and	Increases in 48% of SM, for those PUF with 1 wt.% of GO in compared with PUI foam, increases in density from 490 (neat foam) to 535 kg/m^3, for 1.5 wt.% of GO and increases in T_g from 22.8 to 29.2, for those with 1 wt.% of GO

Table 2 (continued)

References	Graphene type	Amount	Polyol/isocyanate type	Impregnation technique	Foam type	Mechanical/dynamical mechanical or acoustical property and density or specific mechanical property
[33]	rGO	1, 3 or 5 coatings of rGO solution	Commercial low density FPUF	GO dispersed into aqueous solution and the PUF was immersed in it	Open, spherical	Density was not specified. Increases in CM and CS for the foams with a higher layer of the coat. Increases in relative resilience with the increase in compressive strain
[34]	GO	Solutions containing 20 mg/ml of GO	Commercial propylene glycol/toluene	GO deposited on the PUF surface by a vacuum-assisted process	Open cell, medium density (≈31.3, 40.8 and 50.5 kg/m^3), flexible PUF	Averaged sound absorption coefficient (α≈ 800—6300 Hz) increased more than four times by impregnating 15 wt.% of GO into 5 mm thick PUF. CM increased from 57 to 805 kPa upon GO loading of 22.8 wt% (31.3 kg/m^3). The value was increased from 127 to 2311 kPa (50.5 kg/m^3) foam upon GO loading of 11.8 wt%
[22]	rGO	0.25, 0.5 and 0.75 wt% of rGO, related to FPUF	Polyether polyol/MDI	Mechanical stirring of rGO and sonication into the polyol (20 min)	FPUF, open cell, high density (≈100 kg/m^3)	Increases in T_g from –31 (neat FPUF) to –22 °C (FPUF with 0.75 wt.% of rGO)
[35]	EG	0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 2.00, 2.50 wt.% in relation to MDI	Modified castor oil/MDI	Sonication of EG into the MDI	High density, closed cell RPUF	Increase in density from 93.3 to 145.9 kg/m^3. Increase in CM from 5927 (neat RPUF) to 8655 kPa (0.50 wt.% of EG). Increase in toughness from 121,980 (neat RPUF) to 136,000. CS from 420 (neat RPUF) to 467 kPa (0.50 wt.%). Decrease in T_g from 90 (neat RPUF) to 20 °C

Table 2 (continued)

References	Graphene type	Amount	Polyol/isocyanate type	Impregnation technique	Foam type	Mechanical/dynamical mechanical or acoustical property and density or specific mechanical property
[36]	GNPs and NiO	0.5, 1.0 and 1.5 wt.% of GNPs in relation to RPUF mass. NiO was also varied	Polyether polyol grafted with styrene acrylonitrile molecules pMDI	Mechanical staring of both fillers	Semi rigid, closed cell, high density RPUF	The work focused on the improve in fire resistance. However, increases on TM and TS, respectively, from 8.8 MPa and 0.31 MPa (neat RPUF) to 17.3 MPa and 0.43 MPa (1wt.% of GNPs). Increase in density from 29.04 (neat RPUF) to 39.05 kg/m^3 (1.5 wt.% of GNPs)
[37]	GO	1 phr	Commercial/not specified	Two roll-mill mixing technique	Closed cell, high density with low porosity foams	Increase in density from 0.58 (neat PUF) to 0.70, for the foams modified with ionic liquid (IL)-GO. Increase on the CS from 0.16 (neat PUF) to 0.17 (PUF with 1 phr of GO) and 0.30 MPa (PUF with 1 phr of ionic IL-GO)
[38]	Hybrid of GO and POSS	2, 4 and 6 deposition cycles of GO-POSS solution	Commercial, low density FPUF	Layer-by-layer self-assembly technology. Solutions with a concentration of 4 mg/L	Low density, open cell structure FPUF	Compared with pure FPUF, the tensile strength of FPUF@GO/OA-POSS-6 is increased by 42%, and after three times of compression, the compressive strength increases by 83.17%
[39]	GO	0.02wt.% of the foam	Commercial/not specified	Ultrasonication of GO with isocyanate. 24 kHz, 400 W	Closed cell RPUF	Increases in CM from 1115 to 1138 MPa, depending the Aluminum honeycomb used. Slight increase in density from 206 to 209 kg/m^3
[40]	GO	0.05, 0.1, 0.4 and 0.7 wt.% of GO. 1, 3 and 5 wt.% of graphite	Commercial polyether polyol/MDI	Mechanical staring of both fillers	Closed cell, medium density RPUF	Increase in CS from 1.421 to 1.56 for 0.05 wt.% of GO. No information about apparent density

Table 2 (continued)

References	Graphene type	Amount	Polyol/isocyanate type	Impregnation technique	Foam type	Mechanical/dynamical mechanical or acoustical property and density or specific mechanical property
[41]	GO	Solutions with 0.05, 0.1, 0.2, 0.3 and 0.4 wt%	Commercial open cell FPUF/not specified	Dip coating or layer-by-layer impregnation of a PU water based/GO solution	Open cell, low density FPUF	Increases on CM from 48 (neat PUF) kPa and CS from 3, 4 kPa to 265 kPa and 16, 5 kPa (PUF with 0.2wt% of GO). slightly increase on E'. Negligible increment on density when GO is used with PU coating, but a significant increase when PU coating is used
[42]	GNPs	0.1 and 1.0wt.% of GNP in relation to TPU mass	Polyester based TPU	Sonication of GNPs into DMF/TPU solution	TPU foam expanded by $scCO_2$	Decrease in density (0.03vol.%, 0.66 g/cm^3) and after increase (0.31 vol.%, 0.71 g/cm^3) related to neat foam (0.69 g/cm^3). Increase in TS from 12.5 (neat TPU) to 15 MPa (1.0vol.%)
[43]	GO	Commercial PUF		PUF immersed in an aqueous solution of 2 g/L and 4 g/L GO/freeze using liquid nitrogen/freeze-drying	Graphene oxide-polyurethane hybrid aerogel	flow resistivity increased as the concentration of graphene oxide in the sample increased and as the graphene oxide layer became denser. increase in graphene oxide loading increases the mechanical strength of all samples
[44]	Few-layer GNPs	Amounts of GNP/pMDI dispersions with different GNP contents (0.1, 0.2, 0.3, and 0.4 wt% in pMDI)	Aromatic amine-based polyol/Polymeric diphenylmethane diisocyanate	Mechanical stirring	Spherical and polyhedral closed cell	cell contents of the RPUF nanocomposites tended to increase with the GNP content. thermal conductivity of GNP/RPUF nanocomposites decreased. compressive strengths were increased with increasing GNP content and leveled off above 0.2 wt%

Table 2 (continued)

References	Graphene type	Amount	Polyol/isocyanate type	Impregnation technique	Foam type	Mechanical/dynamical mechanical or acoustical property and density or specific mechanical property
[19]	GO/GNPs	GO or GNPs was dispersed in polyol/silicone oil and water at 1.0, 2.5 and 5.0 wt%	Polyol/methylene diphenyl diisocyanate (MDI)	Mechanical stirring	Inhomogeneous open cell structure composed by quasi-spherical interconnected pores	incorporation of GNPs and GO fillers decreases the porosity and pore size. the compressive strengths and compressive modulus steadily grow with the increase in both nanofillers content

CS:compressive strength, TS:Tensile strength, CM:Compressive modulus, SS:Specific strength, Sm:Specific modulus, D:density or apparent density. E' is the storage modulus at the glassy state, *Tg* is the glass transition temperature. DMF is N,N'-Dimethyl formamide. POSS is the polyhedral oligomeric silsesquioxane

3.4 Filled polyurethane foams with carbon structured reinforcements

As already mentioned, the addition of reinforcement in polyurethane foams brings benefits to their properties, as it modifies their morphological structure. Fillers, in a general way, also influence directly on the aforementioned foams' expansion kinetic parameters and consequently on the final foams' cell structure [50]. Bio-fillers, such as those from waste plays an important role on the manufacturing of PUF [51]. On the other hand, fillers with low dimensions and a high content of hydroxyls on its surface plays an important role for the higher thermal instability and PUF's mechanical properties.

Kerche et al. [8] used micro-fibrillated cellulose to improve mechanical properties and thermal stability of a rigid, closed cell polyurethane foam. CO and glycerin were used as polyols and MDI as catalyst. Zhou et al. [9] compared the behavior of semi-flexible PU foams, produced from palm oil polyol (BPU) and CNC, as reinforcement, and a polyester from petrochemical industry (PPU). According to the study, PPU foams presented thicker cell walls and cell struts, and both aspects were larger than those of the BPU foam. The compressive strength (10% deformation) of BPU foam is lower than that of PPU foam, 54 and 125 kPa, respectively. However, with the addition of 4 phr of CNC, there was an increase ~ 50% in the compressive strength of the BPU foam with 4 phr of CNC (117 kPa).

In the same way, graphene (Gr) is a material with detrimental aspects, regarding its use as additive for improvements in thermal, mechanical, anti-fire resistance and thermal insulation of PUF [52]. There are several types of Gr and its specific applications is very related to the type, source and Gr obtention route. For instance, graphene nano platelets (GNP) generally come from powder flake graphite, obtained by exfoliation into a combination of ammonium persulfate, sulfuric acid and fuming sulfuric acid [53]. Neutralization, quenching with water, filtration and washing are also steps used to produce GNPs.

According to Fig. 3a, it is noted that 58% of the articles selected in this review use graphene oxide (GO) as a reinforcement for polyurethane foams. GO is a type of graphene with different characteristics, and consequently, properties. GO presents functional groups, such as hydroxyls and organic acids on its surface, providing characteristics such as high polarity and compatibility with many systems, such as polyurethane.

Multi-walled carbon nanotubes (MWCNTs) and GNPs can also be use as reinforcement into PUF due to their superior properties like GO. Wu et al. [26] established the synergistic effect of different GNPs (in fillers from 0.25 to 0.75% by weight) with MWCNTs in PUF. The results showed a higher synergistic effect with a low content of nanofiller (0.25% by weight), whose tensile strength was improved by about 43%, compared to pristine PU.

In the study carried out by Jia et al. [20], who produced RPUF with the addition of nano porous graphene, they obtained an improvement in morphology and mechanical/thermal properties compared to non-reinforced foam. By adding NPG, the average cell size was reduced and the mechanical properties were affected. When using 0.25 wt.% of NPG, the compressive strength and compressive modulus were increased by 10.7% and 66.5%, respectively.

3.4.1 Strategies to decrease the particles' agglomeration

Due to the well-known trend of graphene agglomeration and formation of clusters, many authors have been developed techniques to avoid this issue. The using of nano or micro particles to increase the distance of GNP or GO is an interesting technique. In their work, Liu et al. [42] used hybrid fillers, composed of Hollow glass microspheres (HGMS) functionalized with silane and used the fillers to improve the composites' compression properties and the lateral compression deformation. Li et al. [22] used Fe_3O_4 nanoparticles aiming to intercalate GO layers with high grafting ratio, resulting in complete exfoliation of GO in matrix.

From the composite foam point of view, the average cell size, cell wall thickness and apparent density gradually decreased along magnetic field direction, forming gradient cell structure in foam. The aforementioned techniques facilitate the dispersion and also the manufacturing of the PUF, since no additional step for the filler dispersion (as sonication) were required. Figure 4a presents the aforementioned strategies, for the improvement of dispersion of graphene.

Li et al. [55] also used a GO functionalized with Isophorone diisocyanate (IPDI), aiming to functionalize the GO surface (Fig. 4b). According the authors, these —NCO groups on the surface of modified GO could participate in the reaction of RPUFs through reacting with polyols to form polyurethane (PU) bonds, then, the mechanical and thermal properties were improved, due to the grater nanocomposite's interfacial characteristics. Other study also used a functionalized GO, with APTES. The authors focused in the improvements of flame retardancy of RPUF with the silane treatment. Despite the improvements in these characteristics, decreases in mechanical properties, when the foams were compared to the neat RPUF were reported regardless a better interactions between GO and RPUF [55].

3.4.2 Techniques for the filled graphene PUF' manufacturing

3.4.2.1 Mechanical stirring and sonication One of the most used techniques for the incorporation of carbonaceous particles in PU foams is the addition of the same directly to the polyol or isocyanate, using mechanical agitation and/or sonication (see Fig. 3c). These are simple and easily manipulated techniques for the production of foams. Different formulations of PU foams are found in the literature, usually the concentration of carbonaceous structures used is from 0.25 to 5% [1, 18, 19, 21, 34, 38, 39, 43].

Another strategy is to disperse the nano particles into the blowing agents, such as Hui et al. [31]. In the study, the authors sonified GO into pyromellitic dianhydride (PMDA). Afterward, TDI was added and under vigorous stirring. Although the increase in density for all contents of GO studied, the authors obtained increases in mechanical and dynamical mechanical properties, as well as in T_g.

3.4.2.2 Dip coating and layer-by-layer impregnation of graphene An interesting alternative, used by some authors, is to coat the foams with graphene solutions. According Li et al. [15], hierarchically nano-architectured graphene-polyurethane hybrid foams can be developed, depending the impregnation technique used for such purpose. A sound-absorbing material may be developed and different cell structures can be formed (varying from Wavy to Web foams` cells), depending the technique used to coat the foam, as presented in Fig. 5.

Oh et al. [15] also used an aqueous solution of GO, using different ratios of compressibility (10 and 20%), for the manufacturing. Compared with neat FPUF the foam interconnected with 2D corrugated GO shows a sound-absorbing capacity of 99.7% at a frequency of 2,236 Hz and a shock energy absorbing time of 189%, during the impact loading. Figure 5 presents the cells` morphology of such foams.

Others studies also addressed this interesting technique, however, using a silicon-based resin, with GO dispersed. Wu et al. [54] reported improvements of fire resistance of 14.7% for the pure foam to 31.5% for PU-RGO–SiR. Moreover, stable electrical conductivity and high flame retardancy, even in a variety of harsh conditions (high temperature, flame, organic solvents and external compression) were reported. Indeed, coatings, using graphene as filler is a new strategy to enhance mechanical, thermal and fire resistance of PUF. Furthermore, self-healing is an interesting characteristic achieved, when these techniques are employed [56, 57].

Meng et al. [15] obtained self-healing FPUF with polyelectrolyte complex coating for flame retardant and also enhanced mechanical properties. Using polyethyleneimine dissolved in deionized water and added to ammonium polyphosphate and subsequently adding GO into the solution, the authors reported a product with the capacity to self-repair even after the destructive mechanical tests.

According to Jia et al. [37] the principle of the layer-by-layer process is to arrange materials of opposite

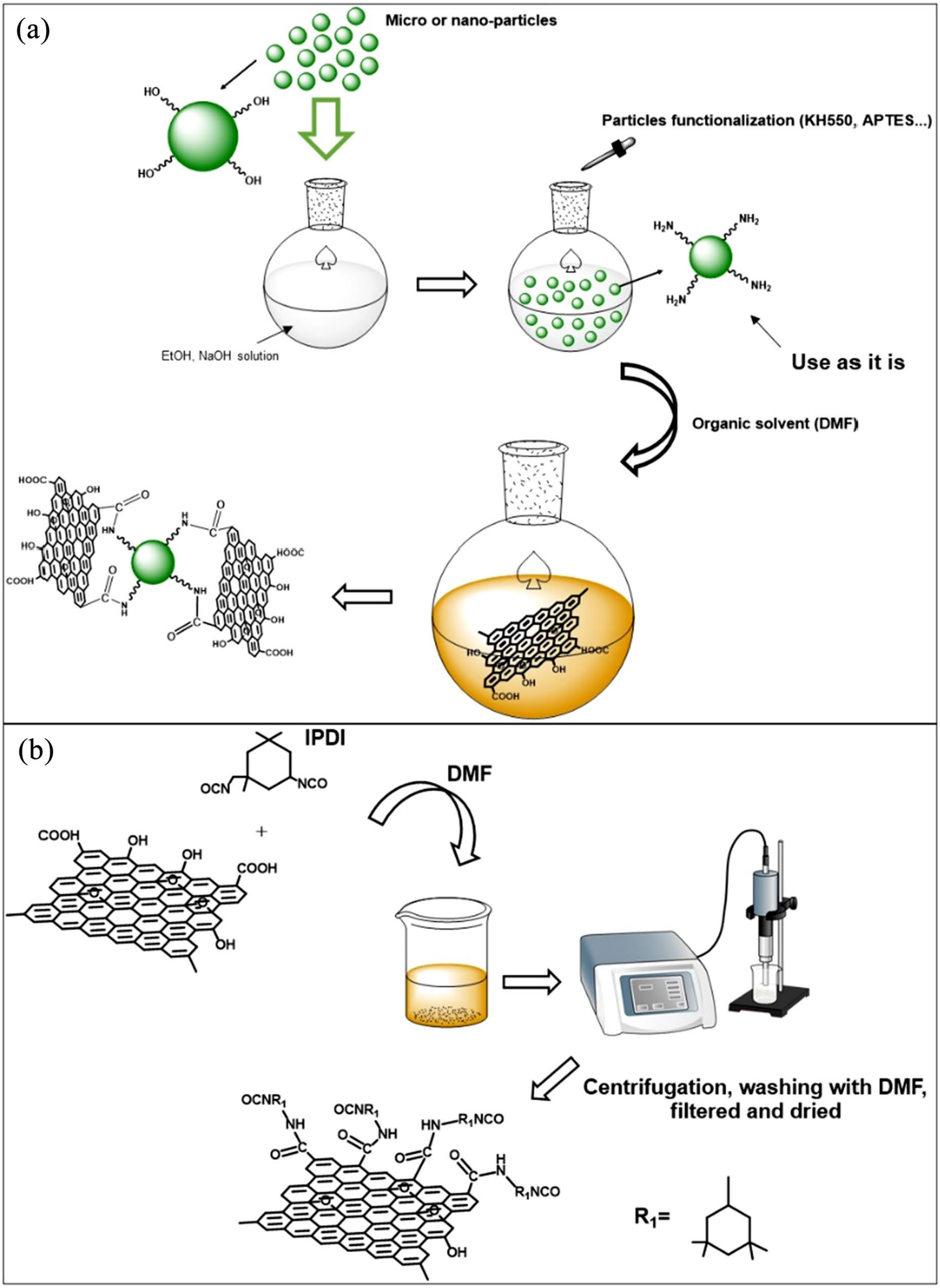


Fig. 4 Schematic diagram of GO nano or micro hybrid filler preparation and functionalization. Adapted from: [15, 23, 54, 55]

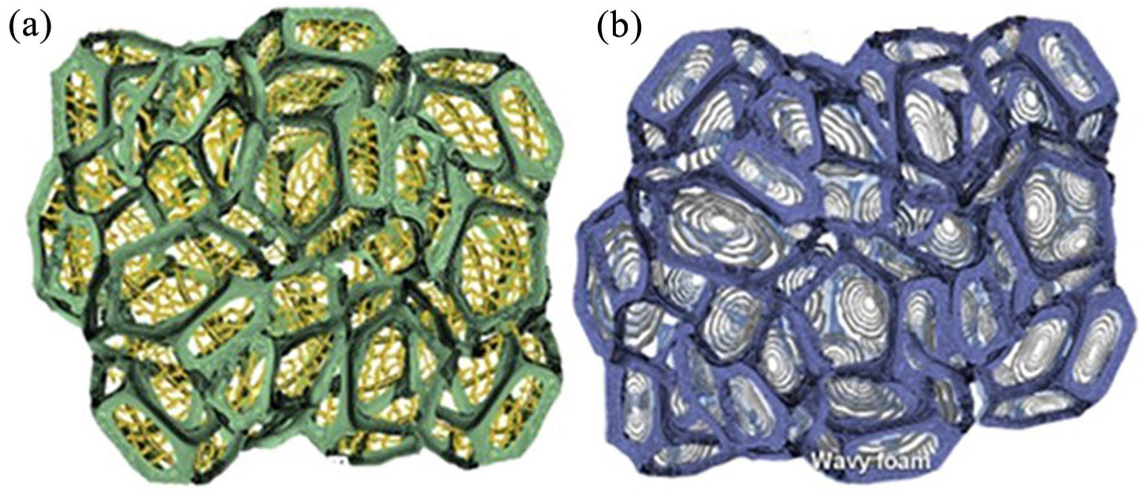


Fig. 5 Cells` morphology of hierarchical porous graphene-polyurethane foams. **a** Web-disordered lattice graphene foam. **b** Wavy-ordered lattice graphene foam. Adapted from: [15, 27, 29]

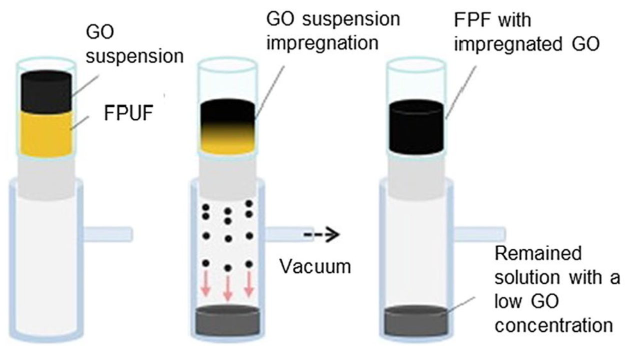


Fig. 6 Aqueous solution for the coating using the layer-by-layer self-assembly technique of graphene on the PUF surface. Adapted from [28, 30, 33, 55, 58]

charge into multiple bilayers so that they are connected and assembled through a variety of attractive forces (such as van der Waals forces, electrostatic bonds and hydrogen bonds). Also, this method is a very effective and environmentally friendly technology for depositing flame-retardant coatings without sacrificing beneficial FPUF properties.

Figure 6 shows the process of impregnation of GO in PU foams carried out by Hou et al. [30]. Basically, the GO solution was poured over PU foam, after which negative pressure (–5 kPa) was applied. After complete immersion of the foam in the solution, the GO-impregnated PU foam was dried in air for one day. This step iterated up to 5 times to increase amount of GO impregnation.

3.4.3 Sound mechanism improvement by graphene using

PU foam is widely used in acoustic materials due to its superior sound-absorbing properties, vibration damping and robustness. In this application, two main mechanisms of acoustic energy damping can be considered. In the automotive industry, there are several different frequency intervals, from those that originate at engine rotation (5–50 Hz), to vibrations generated on irregular road surfaces (500–3000 Hz). So, PU foams are widely used to absorb sounds and noise and thus provide acoustic comfort in the interior of the car [28, 33].

Basically, there is two main mechanism that govern the acoustic energy damping. The first one is related to the sound energy dissipating by the friction between the air gas molecules oscillating inside the foam cells. The air friction can convert the kinetic energy into heat that need to be dissipated by the cells' skeleton. Then, the cell's morphology (open or closed cells' content), stiffness and its capacity to dissipate heat are the primarily responsible for the amount of sound energy absorbed. In the same way, the other mechanism is related to the cell wall material that absorbs sound, also called Intrinsic damping. In this mechanism, the sound waves propagate within the material, where the main factor that influences the sound absorption in flexible PU foam is flow resistance, based on the measurement of airflow resistivity [29].

As reported in this systematic review, the PUF sound absorption capacity may be greatly improved by incorporating particles into the PUF before or after manufacturing [34]. For this purpose, carbon nanotubes [59], silica [60] and graphene [15, 27, 33, 42] are the nano fillers that presented better properties for the improvement on PUF's sound absorption capacity.

OH et al. [42] studied an antagonistic graphene oxide-polyurethane hybrid aerogel with aligned pores and graphene oxide face sheets as a novel sound absorber. The authors reported that the developed material presented a high sound absorption ability due to the effect of graphene nano layer. According the authors, the wave propagation was absorbed by the principle of thermal damping and viscoelastic frame damping, when passing through graphene oxide and polyurethane microcellular structures. Furthermore, tortuosity in wave propagation on the graphene oxide surface and microvibration of narrow GO layers with heat extraction also influences on the sound absorption at low frequencies.

Another issue explored by the authors was the influence of PUF cells' anisotropy on the dissipation of heat that comes from the air friction, as aforementioned. Figure 7 presents the mechanism for the perpendicular (Fig. 7a) and parallel (Fig. 7b) sound energy reflection or absorption on the cell structure, for the developed Gr–PUF. The foams here represented are subjected to the tube impedance test aiming to measure the sound absorption coefficient (α).

Perpendicular G–PUF will produce wave reflections and transmission while passing through the GO layers. In addition, as the sound waves enter, the gaps between GO walls, the fluctuation of acoustic pressure will induce micro-vibration of aligned GO layers [43]. On the other hand, when the foam is positioned with cells parallel to the wave propagation (Fig. 7b) the sound absorption principle follows the mechanism of entering of sound wave enters to the inner void. Here, multiple scattering phenomena strongly reduce the intensity of an acoustic wave passing through the highly porous GO–PUF, resulting in greatly increased sound absorption. Besides, as the sound waves approach the narrow gaps between the GO layers, the air starts to oscillate considerably, and the kinetic energy of the sound waves is lost to friction between the air and the GO layers and to the micro-vibration of the graphene layer [43].

4 Conclusions and future perspectives

This systematic review brings the newest technologies about graphene-modified polyurethane foams. Different types of foams may be manufactured by the use of graphene and its derivatives. Rigid or flexible foams can be reached, depending the chemicals used for the foams' synthesis, additives and technique for the PUF expansion (freely expanded and using a closed cavity). In the same way, the use of graphene may be a benefit, depending the properties desired, which is related to the foam type required for each application (flexible or rigid).

As presented, the deposition of graphene, following layer-by-layer technique is an interesting alternative for foams with high damping properties. On the other hand, sonication and other dispersion techniques for graphene on the polyol are required, when a foam with a high stiffness is desired.

Bio-based polyols were used in many studies. However, new technologies to synthesize foams with polyols from renewable resources are still required, main when a high performance PUF is desired.

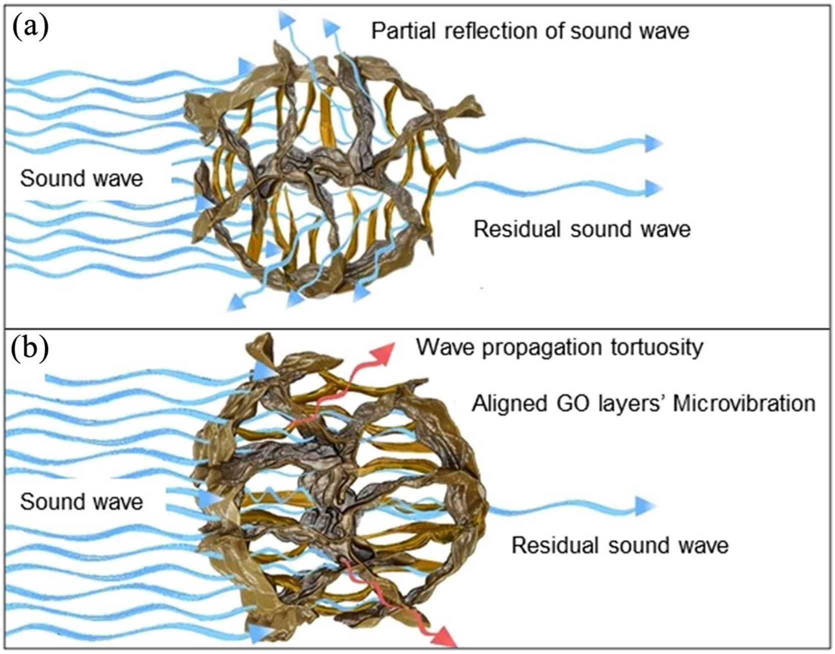


Fig. 7 Representation of the cells with graphene oxide incorporated and the mechanism for the sound wave propagation for the cells oriented perpendicular to the sound wave emission (**a**) and parallel to the sound wave emission (**b**). Adapted from [43]

Finally, it was presented that the sound absorption as well as mechanical properties are high dependent on the direction of property analyzed. Due to the high anisotropy of freely expanded polyurethane foams, its cells growth influence directly on the property direction measurement. Then, its destination and product design need to take into account these issues.

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Declarations

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Informed consent None.

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