PREPARATION METHODS OF GRAPHENE TEXTILE COMPOSITES FOR AUTOMOTIVE INDUSTRY

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Abstract

This is a short review focusing on graphene addition in synthetic fibers of engineering textiles for automotive industry. Graphene has been provided the development of innovative fabrics in order to enhance properties towards smart textiles. These fabrics are composites composed by synthetic polymers as matrices, graphene as reinforcing agent and many additives which introduce functionalities with synergetic effect in graphene incorporation. Methodologies to achieve a successfully graphene addition in textile composites are described and compared such as deposition in the surface of the yarn/fabric by dipping and padding processes, spraying and printing as well as graphene incorporation by solution mixing, melt mixing and in-situ polymerization methods followed by spinning. The properties and potential applications of these composites as textiles for automotive industry are presented. The challenges and perspectives for the next development steps are discussed.

Background

The automobile manufacturers have been looking for newer lightweight materials in place of conventional steel to achieve weight reduction which helps in decreasing fuel consumption and subsequently the CO_2 emission [1,2]. A vehicle weight reduction by a mere 10% improves the fuel economy by 6-8% [3]. Thus, graphene reinforced composite is one of the candidates for textiles in the automotive industry due to its outstanding properties, besides being a lightweighting material. Some applications of textiles in automotive industry can be found in seating fabrics, carpets, curtains, webbings, interior package tray, interior door, airbags, tapes and cords, weather strips, some of them are shown in Figure 1.

Graphene (G) is a 2D material consisted of honeycomb packed sp^2 carbon atoms, having a large surface area, flexibility and transparency, as well as excellent mechanical, electrical and thermal properties [4]. Graphene nanoplatelets (GNPs) are commercially available from single or few layers to nanostructured graphite and their thickness ranges from 0.34 nm to 100 nm. GNP has electronic conductivity while graphene oxide (GO) is an insulator. However, GO sheets are more compatible to organic polymers and solvents due to the higher presence of oxidized functional groups. Partial conductivity can be restored due to partial restoration of the sp^2 carbon structure with acid treatments (as ascorbic acid) to form the reduced oxide graphene form [5].

Figure 1: Some potential applications for textile composites in interior car body.

Source: Adapted from [2022 Ford Bronco™ SUV | Interior Features]

The final properties and applications of the graphene composites are affected by many factors like the dispersion state of graphene and its interfacial interactions with the polymer matrix, the amount of wrinkling in the graphene and its network structure [6]. Graphene tends to agglomerate in composites since graphene layers are stacked together through Van der Waals forces. This graphene agglomeration reduces its specific surface area and consequently the final properties of the composite, being an important issue to be considered in composite production and many techniques have been used to avoid it [7].

Common matrices used for textile composites are synthetic polymers like polyesters (mainly poly (ethylene terephthalate) – PET), polyamides, high molecular polypropylene and polyethylene and natural fibers as cotton, alone or a combination of them and mixed with resins and additives [8]. Graphene (G) reinforcement in textiles can be employed as nanoplatelets (GNP), in its oxide form (GO), reduced oxidized form (rGO) or as graphene fibers (Gf) [5,9]. The oxide form (GO) is usually used when functionalization with matrix is desired due its hydrophilic character assigned to the presence of oxygen functional groups that induces high dispersibility in water or other polar solvents such as ethanol or dimethylformamide (DMF) [9].

Properties and Preparation Methods of Graphene Textile Composites

Many properties have been improved in textile composites due to graphene incorporation such as: anti-static, flame retardant, antiviral and antibacterial properties, UV protection (weatherability), mechanical properties, thermal and electrical conductivity, lower abrasion, shape memory (self-healing), lightweight and flexibility [4, 5, 6, 9, 10, 11]. Figure 2 shows some of them. Self-healing effects render the textile to reconcile its original properties. Moreover, such textiles have capability to sense the damaged place and recover the damaged fabric part [11].

It is important to emphasize that the preparation methods for production of graphene textile composites are adaptations of traditional composite production methods as well as textile production methods.

Among the innumerous production techniques of graphene/polymer composites, solution mixing is one of the most used for the large-scale production [4,10] which includes generally three steps: (1) dispersion of graphene in a solvent via sonification, (2) incorporation into the polymer and (3) removal of the solvent by distillation or evaporation [12]. In step 1, the preparation of stable graphene dispersions is still under investigation and surfactants and polymers can be used [12]. The step 2 which comprises the incorporation of the emulsion of graphene obtained in step 1 is performed by mixing it with the polymer matrix in the same solvent or a combination of solvents via shear mixing or stirring process. The solvent removal in step 3 is a critical issue [12,13]. Further, spinning technique is used to produce yarns through twisting and stretching the composite fibers obtained via spinneret.

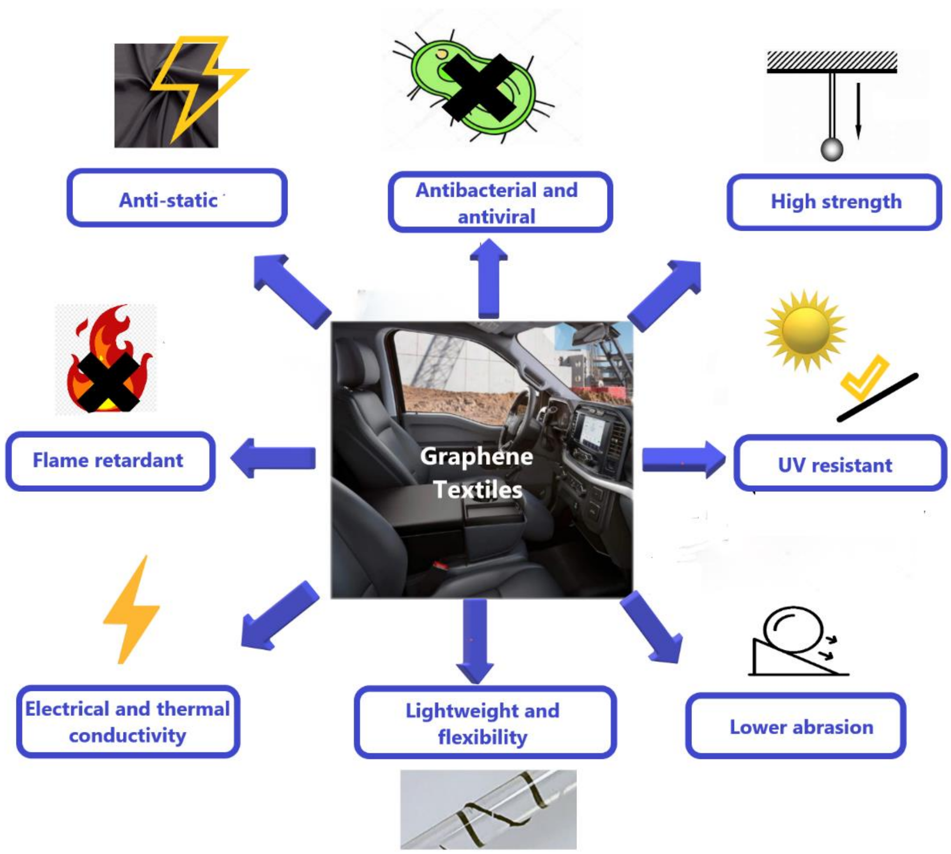

Figure 2: Properties of graphene textile composites.

Source: Adapted from 2022 Ford F-150® Truck | Ford.com.

Melt mixing, followed by spinning, is another common process where graphene and its derivatives are integrated with the molten polymer matrix generally using a twin-screw extruder. In this process, the use of masterbatches (pre-mixtures) to improve graphene dispersion into the polymeric matrix is a common practice [14, 15]. Some drawbacks are related to this process such as heterogeneous dispersion of graphene probably due to the high viscosity of graphene–polymer dispersion, breakage and poor conductivity of graphene sheets due to the higher shear forces [14]. Some authors have already formulated a combination of solution and melting processes [15].

The dipping approach is a low-cost technique that basically consists in coating yarns or the fabric with graphene and its derivatives [6]. It was reported that this technique produces homogeneous films by fabric immersion in coating bath tanks. Bath conditions like pH, temperature and number of cycles of "dipping-drying" process are controlled in order to enhance mass loading of graphene nanosheets [16, 17]. Another way of obtaining graphene coating in fabrics is by ultrasonic spraying of graphene suspension or even film over the fabric covering the whole fibers providing a uniformly coated surface [18].

Padding process is a simple and readily scalable method of impregnating graphene in fibers of the fabric. Graphene-based dispersions were injected into the textile fibers when they pass through a series of rolls that pressed them. This is a common process in textile industry during dyeing process. It is generally used a further step of cure (reticulation) of the polymeric resin (as epoxy resin) that can be present in the graphene-based dispersion. This procedure which uses temperature for polymer curing enables the formation of covalent bonds among the chemical species that favors graphene incorporation and its dispersion. The cycle of the pad-dry-cure process is repeated as many times as desirable to attain the optimum graphene concentration in fabric. This is known as "layer by layer" process [19, 20].

A reactive inkjet printing (RIP) was reported as an useful method for the deposition of reduced graphene oxide (rGO) layers on different textile fabrics that produced conductive textiles using water-based inks with potential uses for electronic textiles [19]. The printing method promise mass customization, decreased material waste, high precision printing and compatibility with a variety of polymeric substrates [21].

In-situ polymerization method is used to incorporate insoluble/thermally volatile materials into polymer matrices that cannot be used in a solution or melt mixing procedure. A liquid monomer is mixed with a filler and then it is polymerized. The graphene precursors and monomer are dispersed in a particular solvent before being ultra-sonicated to ensure that the solution is uniform and evenly distributed [5, 22, 23]. After polymerization reaction, the composite is pelletized. This technique suits uniform dispersion and suitable graphene exfoliation and promotes strong interfacial attraction among graphene, polymer and additives.

Also, authors have already reported the graphene incorporation in polymer fibers through different spinning methods like wet-spinning, melt-spinning, and electrical-spinning [6].

Table 1 shows some considerations of the main preparation methods of graphene textile composites.

Thus, many production methods and a combination of them have been employed to obtain graphene textile composites. The graphene concentration employed in composite manufacture is usually low from 0.1 weight% up to 5 weight% [14,15,22,23]. The graphene agglomeration must be avoided by using appropriate organic solvents in solvent mixing method, selecting suitable combination of dispersion and scalable production method and functionalizing fillers (coupling agents). The use of hybrid fillers as synergistic effects can cause an improvement in the dispersion state of the graphene as metallic nanoparticles (AgO, ZnO and so on) [24].

Functionalization is one of the most used strategies to improve graphene dispersion in polymeric matrix. There are basically two main types of functionalization: (1) chemical functionalization and (2) physical functionalization. Chemical or covalent functionalization can be achieved through the in-situ polymerization method by grafting graphene in polymer matrix through covalent bonding. In-situ polymerization produces high grafting density, but it is highly sensitive to operational parameters. Also, chemical functionalization can be achieved using fillers that are functionalized with suitable functional groups which are then chemically reacted to form a strong bond between graphene and the polymer matrix [5, 6,7]. Silane and titanate agents are commonly used for this functionalization [7,23,24,25].

Table 1: Considerations of Some Graphene Textile Composite Preparation Methods

Graphene Textile Preparation Methods					
Incorporation Methods			Coating Methods		
Solution Mixing	**Melt Mixing**	**In-situ polymerization**	**Dipping**	**Padding**	**Printing, Spraying**
Easy scalable Needs solvent compatible with graphene Needs a stable graphene dispersion Solvent removal is an issue	Graphene dispersion is a challenge Graphene damage due to high shear forces Usually uses masterbatch and reactive extrusion Poor spinning properties	High degree of graphene grafting Strong interfacial attraction Needs rigorous parameters control Needs polymerization chamber	Easy scalable Low cost Needs multiple cycles to high content of graphene Adhesion must be improved	Easy scalable Low cost Needs multiple cycles (layer by layer) A further cure step is used to improve adhesion	decreased material waste high precision printing Needs stable graphene dispersion in ink Adhesion must be improved

In physical or non-covalent functionalization, surfactants are used to functionalize graphene, being physically adsorbed on the surface, decreasing its surface tension and consequently the driving force for the formation of aggregates [7]. Both ionic and non-ionic aqueous surfactant solutions can be used in low concentrations. Mostly used surfactants include sodium dodecylbenzene sulfonate (SDBS), sodium dodecyl sulfate (SDS) and sodium deoxycholate [26].

Although physical functionalization preserves graphene structure, the interactions between functionalities and graphene surface are relatively weak. Thus, it is unsuitable for applications that request high strength where robust molecular interactions are essential [5].

Summary and Next Steps

In this work, it is possible to find some of the recent developments for graphene addition in textile composites. Graphene has proven to have outstanding properties that need to be incorporated at some extent to graphene composites. Many challenges need to be overcome to achieve its maximum potentiality. First, the production of the raw material, graphene, must reach the required quality for scalable production of composites, showing minimum defects like structural wrinkles and impurities. Focusing on high performance graphene textile composites, the next steps are also the accomplishment of better graphene dispersion, strong polymer/graphene interface/compatibility, better composite processability and higher mechanical and viscoelastic properties.

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