Review Article

A Perspective on the Potential Material Candidate for Railway Sector Applications: PVA Based Functionalized Graphene Reinforced Composite

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Abstract
In this perspective article, the advantages offered by the biodegradable poly(vinyl alcohol) polymer matrix with 2D graphene nano-particles (in the functionalized form) for the innovation of new materials are showcased. Functionalization induces strong covalent bonding on the surface of graphene sheets when heaped in between the polymer matrix; on the other hand, no functionalization holds only the relatively weak van der Waals forces. This bonding type difference in conjunction with the ultrahigh tensile strength of graphene nanosheet makes it a suitable candidate for bearing higher loads, and it has been proposed here to use this innovative material in the railway sector application. Many research articles have been discussed here to understand the chemical mechanisms, as well as a thorough literature review, has been conducted for the same.

Keywords: Composites, Poly(vinyl alcohol), Functionalization, Graphene, Reinforcement

1 Introduction

As composites have heterogeneous structures these present vast opportunities to develop any unique material properties as per the requirement. Therefore, demand is increasing tremendously. Due to unique flexibility in various properties, such as production easiness, corrosion resistance, adaptability, robustness, lightweight, cost-effectiveness, etc, these have become a global topic of research across the world. Composites have a wide application in our day-to-day life varying from sports products to space. Research is now more focused on enhancing their properties as conventional materials do not have desired characteristics like strength, stiffness, etc., composites are gaining more importance. In the last few decades, fruitful and continuous progress has been undergone globally to overcome the shortcomings and to meet the demand of the modern world. Several variations with high performance in this field have been achieved to date. Recently researchers have also begun to actively include sensing actuation computational and communicational features into composites, which are known as robotic materials.

During the 20th century, the use of lightweight composite structures began. In the early 1940's glass fiber reinforced plastics were developed with high structural strength, stiffness, and temperature bearing capabilities up to 200 °C provided by glass fiber and plastic matrix respectively. Because of their lightweight and they were used for railways, car bodies, appliances, boats, etc. [1]–[4]. In the last two decades enhancing the structural efficiency of spacecraft and military aircraft has become a common application field. Nowadays emphasis is focused on cost reduction in the production and operational field. By using the different polymers with strong fiber reinforcements, advanced composites are produced. Requirements like reducing the manufacturing time have led to the development of polymers such as polyether – ether ketone (PEEK), a type of thermoplastic polymer. The use of polymer matrix composites is limited to relatively higher temperatures which can be surmounted by the utilization of composites comprising of the metal matrix. Powder metallurgy methods are used to process these composites. The recent development in composites issue of natural fibers, a step towards eco-friendly design. Using carbon fibers has improved the macroscopic properties of polymer composites. Thus, composites will dominate the future and to attain strength superior to conventional metallic metals, a wise mixture of reinforcement and matrix is desirable [5].

The growing concern towards the environment and issues of recyclability has forced researchers to focus more on biodegradable products [6]. To get sustainable composites that have several advantages over conventional ones, the natural and recyclable fibers which have high mechanical strength, low density, and are non-abrasive, have made it possible [7]–[9]. The use of cellulose fibers as reinforcement began after the discovery of cellulose in 1838. The first thermoplastic composite contained polypropylene (PP), high density polyethylene (HDPE), and polystyrene (PS) which were reinforced with cellulosic pulp fiber in 1987. After that several biodegradable fibers have reinforced many thermoplastic polymers such as poly lactic acid (PLA) and polyvinyl alcohol (PVA), etc. Focusing on the composites applied in the railway sector, glass fiber reinforced composites, steel-concrete composites, wood-cement, etc are currently been applied. Here, the author has proposed PVA-based functionalized graphene reinforced composite as a potential candidate for the same railway sector.

2 What is a Composite Material?

A composite is a material made from two or more materials, such as reinforced plastics, metals, or ceramics with significantly different physical and chemical properties, which when combined (without dissolving or blending them into each other) produces a material with completely different characteristics from the individual components. It consists of reinforcement also known as filler that is discontinuous such as fibers, flakes, particles, and fillers, and a matrix that is continuous such as polymers, metals, or ceramics, thereby providing a material with desired superior properties. When designed precisely the new combined material produced has better properties than that of reinforcing and matrix materials. Composites are such a universal material that can provide properties that are not possible to obtain from any distinct material. Berghezan defines composite as “The composites are amalgamated materials which differ from alloys by the fact that the individual components in composites preserve their characteristics but are combined in such a way to take advantage of their features only and not of their limitations, to obtain a much better material” [10].

2.1 *Functions of matrix in composites*

- Form the craved shape it holds the reinforcement together.
- Guard the reinforcement against the environmental conditions.
- Transmit the load to filler.
- Enhance rupture resistance and shock properties.
- Improve the toughness of the material.

2.2 *Functions of reinforcement in composites*

- Uplift the complete mechanical properties of the matrix.
- Provide strength to the composite.
- Improve mechanical properties like stiffness, strength, etc.
- Improve processability in some cases.
- Enhance the properties like abrasion resistance and hardness.
- Reduce shrinkage.

2.3 *Classification of composites*

A composite consists of two or more distinct phase, which is matrix phase and dispersed phase.

- **Matrix phase**

It is a primary phase that has a continuous character such as metal matrix composite (MMC), ceramic matrix composite (CMC), and polymer matrix composite (PMC) that is further divided into thermoplastic and thermosetting composite.

- **Dispersed (reinforcing) phase**

The second phase i.e. dispersed phase or reinforcement is embedded in the matrix in a discontinuous form such as fiber composites, particulate composite, and structural composites which can be further classified into laminate and sandwich composite.

Composites can be classified under different categories like classification according to their components, the number of layers, fiber direction, fiber length, etc. Composites are mainly classified according to the geometry of a characteristic unit of reinforcement because it is the geometry or structure of reinforcement that is responsible for the mechanical properties and according to the matrix.

2.3.1 Classification according to the matrix

- Metal matrix composites (MMCs)
- Polymer matrix composites (PMCs)
- Ceramic matrix composites (CMCs)

In metal matrix composites (MMC), metal fibers are used for reinforcement as these have low cost and have comparatively high specific mass. Such composites are not highly used because they have high density. Heat resistant metal fibers are used as metal matrices to withstand higher temperatures. Polymers are considered to be an ideal matrix material for composites as these have low density, required mechanical properties, such as excellent strength, high rigidity, are fatigue resistant, and can be easily processed and machined. Therefore, composites based on polymers i.e. PMCs are widely used in various applications. There are two types of polymers namely Thermosets and thermoplastics. Thermoplastics do not undergo heating, they soften or melt to reuse again i.e. their original features can be restored by cooling whereas thermosets polymers form a series, making it difficult to reuse again on heating. These are the most extensively used matrices for advanced composites. In ceramic matrix composites CMCs, ceramic fibers are used. Ceramics have high strength and young's modulus. These are used to improve the fracture toughness of the combined material system.

2.3.2 Classification according to the geometry of reinforcement

- Fiber reinforced composites (FRC)

A fiber-reinforced composite (FRC) is a composite building material that consists of three components:

1) The fibers as the discontinuous or dispersed phase.

2) The matrix as the continuous phase.

3) The fine interphase region, also known as the interface.

In other words, it can be defined as multi-constituent materials that consist of reinforcing fibers embedded in a rigid polymer matrix. Fibers are known for their length and cross-section ratio. For fibers, this ratio must be high i.e. length much greater than that of the cross-section. Fiber's orientation in a matrix indicates the composite's strength and resistance along the fiber's longitudinal direction. Due to their small cross-sectional dimensions, these cannot be used directly for engineering applications. Therefore, their embedding in the matrix is required to produce fibrous composites.

Many FRCs have both strength and modulus which are superior to many conventional materials. In many applications, like aircraft parts, there is a need for high strength per unit weight. This can be achieved by a composite consisting of a low-density matrix reinforced with stiff fibers. This is a type of advanced composite group, which makes use of rice husk and plastics as ingredients. This technology involves a method of refining, blending, and compounding natural fibers from cellulosic waste streams to form a high-strength fiber composite material in a polymer matrix. Various polymers can be used as a matrix to FRC composites which are classified as thermoplastic resins or thermoset.

- **Particle-reinforced composites**

The name, particle reinforced, itself specifies that the reinforcement exhibits particle nature. It may have any shape or size like cubic, spherical, tetragonal, ellipsoidal, polyhedral, or of any regular or irregular shape, but it is approximately equiaxial. Here, particles of one material are dispersed in particles of other materials or matrices. The particles of the first material may or may not be compatible with the particles of the matrix. To establish the compatibility between them, treatments are done so that they can be easily embedded into matrix materials. They may be added to a liquid matrix that later solidifies; grown in place by a reaction such as age hardening, or they may be pressed together and then inter-diffuse via a powder process. The function of particles as reinforcement material is to improve the mechanical properties of composites.

They are of two types based upon strengthening mechanisms at the atomic or molecular level.

1) Dispersion-strengthening

The strength and hardness in some metal alloys may be increased by adding small uniformly dispersed particles within the original phase matrix. The size of added particles ranges from 0.01–0.1 µm, such as fine particles of Al203 in aluminium. It includes interactions between particles and dislocations inside the matrix (Reinforcement happens at the atomic or molecular level, their applications are making rivets and wing plates for aircraft because of enhanced tensile strength and hardness).

2) Particulate-reinforced composites

In this particles of one material (no long dimensions) are dispersed in a matrix of the second material. It contains large quantities of coarse particles that are intended to create a combination of characteristics. It has less strength than fiber reinforcement. The main focus in particulate-reinforced composites is on stiffness but strength and toughness can also be increased. Its application is where high levels of wear resistance required road surfaces. In the present investigation, polymer matrix composite has been fabricated in which thermoplastic polymer has been used as a matrix phase.

3 Polyvinyl Alcohol (PVA) as the Matrix

PVA is known to be favorable material for a variety of applications. It is a granular or powdered semi-crystal or linear synthetic polymer with a creamy look, tasteless, odorless, and non-toxic nature [11], [12]. Besides these, it is thermally stable and possesses amazing optical properties, large dielectric strength, etc. which makes it a good choice as a matrix for optoelectronic applications [13], [14]. It exists in different morphologies. PVA having a chemical formula $[CH_2CH(OH)]_n$ cannot be obtained directly. Its synthesis is a two-step process. Firstly, vinyl ester is synthesized which is further hydrolyzed [15]. By saponifying poly(vinyl ester) with sodium hydroxide solution, it was first synthesized by Hermann and Haehnel in 1924 [16]. For sustainable and recyclable man-made composites, Polyvinyl alcohol has been recognized as a considerable matrix, thanks to its exceptional properties of solubility in water, biodegradability, bio and eco-compatibility, high tensile strength, outstanding adhesive properties, chemical resistance and gas obstruction features [17]–[19]. The use of water solubility (up to 100 g/L) feature of PVA as an advantage or a limitation totally depends on the application for which it will be used. Other than these features, it owns great oil and grease resistance, ecological biodegradability by microorganisms and flexibility. These microorganisms degrade the PVA through enzymatic processes, which results in less environmental pollution. However, it percolates to groundwater from soil without any difficulty thus creating environmental issues due to increased mobilization due to heavy metals resulting in lumps of hazardous materials. It comes in different grades based on the viscosity and hydrolysis's degree [20]. Many experimental studies were conducted on composites having PVA resin that may be used in green composites for applications, such as coating, eye drops, plastics, concrete reinforcement, etc [17]. It proves to have great potential for biomedical applications. It is used with recyclable fibers for making biodegradable composites. For different desired applications, the modification of PVA has become essential. Hydroxyl groups are used to modify it chemically. Various traditional methods used are acetalization, carbonation, etherification of the hydroxyl groups of PVA. The modification of PVA made it possible to use this in applications like molecular sensing, biological and biomedical, fuel cells membrane, chemosensors, absorption of toxic metals and optoelectronic devices. The most important part of composites is a matrix, which must be biodegradable due to increased environmental concern. PVA is one such matrix, which can be easily degraded by microorganisms into water and carbon dioxide molecules which can be utilized by flora [21]. It can form a uniform and high optical quality film which can be used for non-linear optical devices and optical sensors. PVA is mainly used in medical, electronic, paper industries, food industries, civil, drug delivery industries etc.

4 Graphene as a Reinforcing Material

Graphene is a carbon allotrope having a single atom thick sheet of hexagonally arrayed honeycomb structure in which sp^2 hybrid carbon atoms has been under the spotlight owing to its intriguing and unparallel physical properties are arranged which was developed in 2004 by Andre Geim and Konstantin Novoselov with their team [22]. Due to its astonishing mechanical properties, it becomes a decent reinforcement in polymer composites. However, its utilization as reinforcement had begun much late. The strong covalent bond between its carbon atoms is responsible for its outstanding tensile strength (~ 125 GPa) and has a high Young's modulus of around 1000 GPa [23]. It is one of the most robust and stiffest (modulus ~1 TPa) material. Additionally, these carbon atoms have exceptionally high electrical conductivity, high thermal conductivity of order 5000 W/mK [24]. It proves to be one of the best thermoelectric conductors. On the other side, graphene sheets provide a large speculative surface area (2630 m^2/g). These amazing properties make it available for applications like as flexible electronics, quantum capacitors, hydrogen storage devices, chemical sensors, and nano-composites.

Its extension to a large length and width of only 0.34 nm in thickness (up to several nanometers in the case of several layers of it) make grapheme superior over other reinforcing materials. A lot of opportunities have been created for the interface because of its large surface area to toughen the interface with the matrix. The fact that graphene in a polymer matrix has similar characteristics as the filler with a similar micron height prevents the untimely damage of composite materials. It also stimulates the enhancement of ductility and toughness. Thus, graphene becomes a perfect alternative as reinforcement because of its distinctive combination of properties like strength, maximum, Young's modulus, higher viewpoint proportion, high thermal conductivity, etc. To make new, strong, and efficient polymer composites, graphene-based fillers have been used. The characteristics of high available surface area and nano-size thickness with two-dimensional structure can be utilized in load-bearing, electrical, and barrier applications.

Due to the unique characteristics of polyvinyl alcohol like simple and easy processing capacity, bio inertia and transmittance, etc., it has opted as the host material for various research works. PVA has become an optimum choice as a matrix in the areas of electronics, optoelectronics, and biomedicine for forthcoming applications. Thus, for improving both mechanical and physical properties, it will become an attractive alternative for different applications.

Oxide is desirable that a strong bond is usually formed between graphene and the polymer with the help of a covalent bond between functionalization of graphene with PVA. However, it is difficult to know because ideal graphene lacked functional groups that can be conjugated. In many cases when the graphene sheet was exfoliated from graphene oxide incomplete reduction process leaves oxygen containing functionalities that are available for further functionalization.

As we know graphene oxide is the main precursor for functionalized graphene with polymer. It is because there are multiple oxygen-containing functionalities, such as hydroxyl epoxy and carboxyl groups on graphene sheets. The Hummer method is commonly used in which graphene is oxidizing using strong oxidants such as $KMnO_4$, $KClO_3$ and H_2SO_4, and HNO_3 (Most commonly by the solvent-based exfoliation and reduction inappropriate medium or thermal exfoliation and reduction). The chemical reduction of graphene is produced by chemical reduction such as ultrasonication, stirring, and forming colloidal suspensions of graphene. The most promising methods for the large scale production of graphene are the thermal exfoliation and reduction of graphene can be rapid heating of dry graphene under insert gas and high temperature.

The important purpose of functionalizing the filler is to enhance the different mechanical properties of the graphene-based polymer system. With improved interfacial adhesion, supramolecular complexes are formed which further enhance the dispensability of graphene in the polymer matrix. Various methods have been observed to date which disperses the graphene uniformly in a matrix to improve the mechanical properties. By functionalizing (at different time periods for refluxing and vacuum oven) and regulating the preparation conditions, optimized composite properties can be obtained. Experimental results showed that increment of 30–350% in modulus of elasticity and 50–200% increment in tensile strength can be achieved with different polymers.

The highly sensitive biosensors, synthesized by functionalized graphene (which forms an interface with biomolecules) provide new health area advantages. This made a label-free measurement of key bioactive cell molecules, innovative nano-particles for tissue targeted drug delivery, and scaffolds for tissue engineering easy. Functionalized graphene can also be used to attain biological interactions with novel results.

One of the most important reasons for using pure graphene sheet functionalization is to enhance the dispensability in different solvents which led to the advancement in graphene-based nanocomposites. Other advantages of functionalization include modification in the intrinsic characteristics, electrical properties like conductivity, bandgap, etc for nanoelectronic devices. Functionalized graphene bound to the polymer matrix also possesses improved mechanical properties. In general, a range of enhanced mechanical properties can be attained by incorporating and functionalizing graphene fillers. This will change the interface of the different polymerization systems. Functionalization of graphene will comprise some of its natural conductivity this functionalization method is still valuable in some cases when graphene's other properties are desirable.

5 Literature Review

The objective of this section is to provide background knowledge and data on the biodegradable polyvinyl alcohol synthetic thermoplastic used as a matrix material for the growth of biocomposites/nano-composite. The purpose is also to discuss the work on the introduction of functionalized graphene nanocrystals for the regulation of thermal and mechanical properties of polyvinyl alcohol as done by various researchers in the past. It presents a thorough understanding of the various aspects and work that has been done on graphene and polyvinyl and how dramatically their combination as composites changes the properties. The main focus is on the mechanical and thermal properties of PVA-based particles or fiber composites having nano/micro-level reinforcement materials and various polymers used in the preparation of PVA films.

Further review has been done on graphene PVA based films and graphene nanocrystals reinforced composite and functionalization of graphene with different acids (for example: citric acid, H_2SO_4, $KMnO_4$) for activation of functional group (as hydroxyl –OH) for better intermixing between the particles and matrix to achieve stable and uniform distribution of graphene nanocrystal particles in a polymer matrix, and to have enhanced thermal and mechanical properties in the polymer matrix. Various methods have been reported for the research of graphene-based PVA composites with enhanced mechanical, thermal, and electrical properties.

5.1 *Polyvinyl alcohol based composite/films*

Lu *et al.* [25] prepared composite polyvinyl alcohol/micro-fibrillated cellulose in which micro-fibrillated cellulose was used as a reinforcement material. For 2 h at 95 °C, 5 wt% of PVA solution with water was stirred and then micro-fibrillated cellulose (1, 5, 10 and 15 wt%) was added. After it was cooled to room temperature, PVA-based film was tested for its mechanical properties. Observation showed that Young's modulus and tensile strength improve with a loading of 10 wt% of MFC content.

Das *et al.* [26] prepared functionalized few-layer graphene (FG)-reinforced nanocomposite with the use of polyvinyl alcohol (PVA) and PMMA matrix. He used nanoindentation technique to evaluate the mechanical aspects. With the addition of a small amount of graphene having a concentration of 0.06 wt%, properties like crystalline, elastic modulus, and hardness were significantly enhanced. It was supposed that this improvement in mechanical properties happened due to close mechanical interaction between the host (polymer) matrix and the layers of graphene that is responsible for efficient load transfer within the host matrix and the nanofiller.

Liang *et al.* [27] prepared the graphene (Gr)-PVA nanocomposite by using an eco-friendly and simple water solution processing method i.e. water used as a solvent. A considerable amount of load was transferred between the graphene nano-filler and PVA matrix. With dispersion, the mechanical properties of graphene based nano-composite were improved considerably. By introducing a fairly small 20 wt% of f-Gr enhancement of 76% in tensile strength and 62% in Young's modulus was observed. Further comparison between simulated values and experimental results showed that tensile load applied externally was transferred to the graphene sheets across the graphene-PVA interface. This occurred due to the strong hydrogen bonding between them. This study indicates that the processability of functionalized graphene sheets may be utilized for the preparation of various nano-composites.

Naseh *et al.* [28] functionalized the carbon nanotubes using nitric acid oxidation and dielectric barrier discharge (DBD) plasma method. The carbon nanotubes that were used for the experiment were prepared by the method known as chemical vapor deposition (CVD). Heating purification of CNTs was also done under a helium atmosphere to eliminate the acidic functional groups. Fourier transformed infrared spectroscopy (FTIR) has been done to investigate the attachment of functional groups. FTIR shows the formation of oxygen containing groups like C=O and COOH. Results showed that functionalization done by using nitric acid was more destructive in comparison to plasma treatment. Plasma treatment adds a less functional group in comparison to the acidic treatment. It was found that the functionalization done by plasma functionalizes the surface only whereas chemical treatment not only affects the surface but also shows some changes in the bulk of the material.

Salavagione *et al.* [29] successfully synthesized the PVA/reduced graphene (RGr) nano-composites and coagulated the system with 2-propanol. It was observed that some interaction occur in the nanocomposite between the polymer and the reduced graphite oxide layers due to hydrogen bonding formed resulting in alteration in the thermal behavior of the nanocomposites and lower the mean temperature by 35 °C. With 20 wt% of reduced graphene, crystalline dropped to half. Further, with percolation threshold between different time periods for refluxing of reduced graphene, electrical conductivity reached a value 0.1 S cm^{-1}.

Zhao *et al.* [30] successfully prepared graphene based PVA composite by introducing graphene oxide into PVA matrix, thereafter reducing f-Gr into graphene nanosheets. This resulted in considerable enhancement in mechanical properties. For instance, adding 1.8 vol.% graphene nanosheets increased the tensile strength by 150% that showing the efficient transfer of load between reinforcement and matrix. The composite's modulus increased by ten times as compared to parallel PVA sample. Also composites crystalline improved slightly. It was assumed that there might be a critical point up to which properties improve. It was concluded that the graphene nano-sheets might be randomly dispersed in the PVA matrix when the experimental results and Halpin-Tsai theoretical prediction were compared. The challenge that was left was the easy introduction of nano-fillers into matrix and dispersion of graphene nanosheets in large quantitities.

Yang *et al.* [31] reduced graphene in the PVA polymer matrix to prepare layer-aligned poly(vinyl alcohol)/graphene nano-composites films by using a simple solution processing method. F-graphene forms strong interfacial interaction due to hydrogen bonding in the PVA matrix and is dispersed homogeneously at the molecular level. This interaction changes the morphological structure and properties of PVA/f-graphene nanocomposites. Strength (Tensile strength and modulus) and ductility improved while crystalline decreases. The increment in the glass transition temperature decreases the crystallization level. It displays that graphene can be used efficiently as thin two-dimensional nano-sheets within the polymer matrix for large-scale prospective applications for polymer/graphene nanocomposites.

Due to the strong interlayer cohesive energy and surface inertia, control and optimization of interface structure and dispersal of graphene nanosheets in polymer become a new challenge in the preparation of highly efficient graphene-based nanocomposites. Wang *et al.* [32] successfully introduced graphene oxide and graphene into PVA aqueous solution and subsequently reduced graphene to f-graphene sheets in order to develop graphene-reinforced poly(vinyl alcohol) (PVA) composite film. This was a simple and the realistic approach that increases the tensile strength up to 212% and 34% in elongation at break. The water absorption ratio of the f-graphene/PVA composites reduced from 105.2 to 48.8% compared to pure PVA as observed by water absorption measurements. The barrier properties were also improved. The behavior of PVA films changes from hydrophilic to hydrophobic at a low loading of graphene content, which improves the water-resistance of PVA.

Wang and Hsieh [33] studied cross-linking of polyvinyl alcohol (PVA) fibrous membrane with polyethylene glycol (PEG) diacylchloride and glutaraldehyde. It was stated that electrospun aqueous solution of PVA cross-linked with GA and PEG diacylchloride was found to be effective in fabricating water stable hydrophilic PVA fibrous membrane. There was an enhancement in crystalline structure in PVA fibrous membrane cross-linked with GA/ethanol, whereas reduction in crystalline structure in PVA fibers cross-linked with GA in an aqueous solution of sodium sulfate (Na_2SO_4). Complete loss of crystalline structure was found in PEG diacylchloride cross-linked in toluene/pyridine. Reaction with the lower and shorter extent of PEG produced hydrophobic PVA fibrous membrane with minimum change in interferer porous structure, among all cross-linking agents.

Dongil *et al.* [34] investigated surface chemical modification induced on high surface area graphite (HSAG) and carbon nanofibers (CNFs) using functionalization and oxidation treatments. Two oxidation methods aqueous HNO_3 wet oxidation and oxygen plasma oxidation were used. The plasma treatment appeared to be more effective in modify CNFs. The amounts of groups were increased on HSAG by wet oxidation, which was found not so effective for graphitized CNFs.

Guo *et al.* [35] focused on improving the improving tensile strength, modulus, and thermal stability. The water-dispersed graphene/PVA nano-composite was synthesized with the help of tryptophan. Graphene sheets (prepared by reduction of graphene oxide) functionalized non-covalently and stabilized with aromatic amino acid i.e. tryptophan. Tryp-functionalized is water dispersible. Even with a small content of graphene approximately 0.2 wt% results in considerable improvement in mechanical properties. Tensile strength improved by 23% while young's modulus and thermal stability moderately increased as investigated by tensile testing, Atomic force microscopy (AFM), X-ray diffraction (XRD), UV–vis absorption, and Raman spectroscopy.

The fabrication of f-graphene-PVA nanocomposites was done by combining different solution processing and then compression molding [36]. Either graphene or functionalized graphene sheets were blended with PVA. Here the chemical modification graphene was fully introduced into matrix as showed by SEM imaging combined with XRD measurements. This modification averted the particle aggregation and enhanced the reconcilability with the polymer matrix. At f-graphene loading greater than 1 wt%, improvement in thermal stability was observed. Differential scanning calorimetric thermograms showed that with optimum loading of 2 wt%, crystallization of matrix was induced by the f-graphene nano-platelets. Dielectric measurements showed that this system flaunted a trend of degradation in the values of permittivity with filler content. This could be utilized for the formation of an insulating coating between graphite inclusions and PVA.

Morimune *et al.* [37] employed an ordinary solution casting process to fabricate PVA–Gr films. Gr was nano dispersed uniformly in the PVA matrix led to the strong interaction between PVA and f-Gr. With an increase in the concentration of f-Gr nano-filler, it was observed that the properties such as Young's modulus, tensile strength, thermal and barrier properties were improved appreciably. This happened due to the stiff structure and large aspect ratio of individual f-Gr sheets. The results were compared with the model forecast using the Halpin-Tsai equation. Additionally, increments in thermal and barrier properties of the nano-composites were observed.

Cano *et al.* [38] functionalized graphene (Gr) by its covalent functionalization with PVA by esterification of carboxylic group on Gr with hydroxyl group of PVA that results in f-(PVA)Gr. Paper-like material can be formed by functionalized graphene oxide through the vacuum filtration method. There was a significant increase in mechanical properties of paper-like material formed by functionalized graphene oxide in comparison to those prepared with the mixture of Gr and PVA or Gr. They were stiffer and stronger too. In order to form composites, functionalized Gr flakes were dispersed in PVA matrix. Approximately 60% increase in modulus and strength for f-(PVA)Gr of loading below 0.3 volume % was reported.

Zhou *et al.* [39] used a low percolation threshold and high electrical conductivity by using large-area reduced graphene oxide sheets to prepare the poly(vinyl alcohol)/reduced graphene oxide (PVA/Rgr). These large area graphene oxide sheets showed better overlapping characteristics and form a continuous network in PVA matrix in comparison to small area Gr. This is because of their higher aspect ratio. Lf-Gr sheets enhanced the electrical conductivity of nano-composites throughout the thermal reduction process. After being used, these would recover their electrical conductivity as they have a low degree of oxidation. The thermal reduction process proved an efficient and time saving method, taking only 15~30 min to reduce PVA/f-Gr nano-composites efficiently. As a result, the percolation threshold of PVA/Lrf-Gr nano-composites is ~0.189 wt% lower than present reports (0.5~0.7 wt%). With a high concentration of large area f-Gr (0.7 wt%), attainment of electrical conductivity 6.3×10^{-3} S/m was possible. This method helped in shortening the preparation period, simplifying the post treatment, increasing the electrical conductivity of nanocomposites at low f-Gr contents and avoided using the surfactant to redisperse the rf-Gr sheets. Here, Hummers method was successfully employed to synthesize the solubilized f-graphene.

Ramalingam *et al.* [40] used alkaline solution to prepare PVA–f-graphene nano-fibers via electrospinning technique with various loading concentrations (10, 30, 50, 70, and 90%) of graphene and investigated by using Raman spectra, Fourier transform infrared spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Results showed improvement in electrical conductivity with a high concentration of PVA/f-graphene hybrid nano-fibers compared to pure PVA. Composites containing 70% and above ratio of f- graphene can be used for applications in nano-electronics, transparent electrodes, and supercapacitor.

Chitosan (CS)-PVA and f-Gr based nano-composites were prepared by Pandele *et al.* [41] with enhanced mechanical, thermal and bioactive properties which make them suitable for application in bone repairmen and tissue engineering. It was synthesized by casting the stable aqueous mixture of the components. At molecular level, graphene oxide was dispersed homogeneously and some sort of interaction occurred between graphene oxide nano-sheets and CS-PVA (as observed by SEM, TEM and X-ray diffraction). With the introduction of on 6 wt% Gr increased the tensile modulus up to 1.83–5.78 GPa (over 200% increment than neat CS-PVA composites). The obtained composite film was thermally stable at a low loading of f-Gr (0.5 and 1 wt%) and high loading led to a considerable increment in the proliferation rate of the cell.

Montes *et al.* [42] observed an improvement in thermal stability by blending stabilized graphene with an aqueous PVA directly and subsequent casting evaporation. The evaluation showed that 1 wt% graphene-CNC improved the Young's modulus by 50% and tensile strength by 20% as compared to neat PVA. This improvement was significantly higher than those obtained with plain CNC at the same loading level. Here CNC acted as a graphene stabilizer which favors its diffusion in the polymer matrix.

Chen *et al.* [43] focused on improving the mechanical and thermal properties. He used the aqueous solution technique and added boric acid (BA) and f-graphene (f-Gr) and studied the effect of PVA film. Observation showed that with 5 wt% boric acid tensile strength increased from 23.3 MPa to 67.7 MPa and by incorporating 20 wt% f-graphene it further enhanced from 67.7 MPa to 88.5 MPa. Introducing nitric acid and graphene oxide additionally improved the thermal stability.

Jose *et al.* [44] dispersed the graphene efficiently in poly(vinyl alcohol) (PVA)/starch. They did this by using the polymer nano-composite solution mixing and casting method to prepare polymer nano-composite. Glycerol was added to the starch dispersion uniformly as a plasticizer. FTIR studies show that hydrogen bonding was formed between graphene and the PVA/starch matrix. At the loading of 20 wt% PVA, the maximal value of mechanical properties including tensile strength was obtained. With the use of starch and graphene, the thermal stability of PVA was improved while the crystallinity decreased. Further introducing the graphene and blending of starch, the brittle nature of PVA changed to ductile.

5.2 *Functionalized graphene as reinforcement*

Li *et al.* [45] fabricated PVA/cellulose nano-whisker (CNWs)/chitosan nano-composite. At different wt% of chitosan, 1 wt% CNWs and PVA were added. The results obtained for PVA/CNWs and PVA/chitosan were compared. It was found that elongation at break was less for PVA/chitosan (15 wt% chitosan) than neat PVA whereas both elongation at break and tensile strength were increased for PVA/CNWs compared to neat PVA films, which was due to enhancement in the interaction between PVA chains and CNWs through hydrogen bonding.

Anstey *et al.* [46] performed oxidative acidic treatment and characterization of new bio-carbon from sustainable Miscanthus biomass was done by using nitric acid, sulphuric acid and their mixture. Oxidative acid treatment has been used to modify the structure of carbon. Biochar has been introduced to reflux vessel with 70% nitric acid. The solution with constant stirring refluxed for 6 h. The same experiment was performed using 95% sulphuric acid for the treatment of biochar. The FTIR spectrum of treated biochar was compared to untreated biochar spectra. H_2SO_4 treatment resulted in a slight increase in the sample's sulphur and oxygen content. Compared to the spectra of untreated biochar, the new peaks were found in the FTIR spectrum disclosed the addition of carboxylic acid and nitro groups after the treatment of both HNO_3 and HNO_3-H_2SO_4. The treatment with HNO_3-H_2SO_4 has been revealed to be the most effective way to modify the biochar, and will probably provide the best degree of functionality to improve interaction with polymer matrix.

Kashyap *et al.* [47] developed graphene (Gr) reinforced PVA nano-composite. The comparison between neat PVA film and PVA/f-Gr film shows that tensile strength improves from 25.3 ± 3 MPa to 63 ± 5 MPa and Young's modulus from 2.32 ± 0.3 MPa with neat PVA film to 5.82 ± 0.6 MPa with PVA-Gr.

Polyvinyl alcohol hydrogels have limited applications in many fields due to their poor loading. Shi *et al.* [48] prepared PVA/Gr composite hydrogels using the freeze-thaw method to study the effect of f-Gr time on microstructure, water content, mechanical, and tribological properties. It was observed from the results that the f-Gr sheets form cross-linkage with PVA molecular chains to create excellent interfacial interaction with PVA hydrogel matrix. This resulted in enhancing the mechanical properties. Results showed that optimization of f-Gr for different time periods for functionalization with refluxing and vacuum oven increases the tensile and compressive strength by 116% and 161% approximately when compared with neat PVA. The instantaneous pressurization under compressive load would increase as Gr obstruct the water infiltration between the PVA molecules i.e. Gr improves the water locking ability. This further increases the load-bearing capacity. With an increment in Gr concentration, the friction coefficient of PVA/Gr hydrogels decreased. It also enhanced the wear resistance of PVA hydrogel composites.

Ma *et al.* [49] in his paper discussed new and bottom-up in situ polymerization method to synthesize poly(vinyl alcohol) (PVA)/f-graphene (f-Gr) nano-composites. The process is done by mixing vinyl acetate, methanol, initiator and f-Gr with the assistance of high power ultrasound. Further, this process was followed by free radical polymerization and alcoholisms reaction which result in the uniform dispersion of f-Gr in PVA matrix. Hence, a strong hydrogen bond formed. As a consequence, due to the effective load transfer between the PVA matrix and Gr the mechanical properties and water vapor barrier properties of PVA/f-Gr nano-composites improve even with a low loading of f-Gr (0.01–0.08 wt%). Incorporating only 0.04 wt% Gr enhanced the tensile strength from 42.3 to 50.8 MPa, and Young's modulus from 1477 to 2123 MPa. Moreover, the coefficient of moisture permeability declined to about 78%.

Jose and Al-Harthi [50] used the casting method to prepare Polyvinyl (alcohol) / starch / graphene nano-composites in which glycerol plasticizer and citric acid (CA) act as the cross-linking agent. The purpose was to enhance the features. With 20 wt% graphene, the concentration of citric acid was varied and its effect has been studied in detail. It was found that with 20 wt% of f-graphene highest characteristics were obtained like tensile strength has increased from 6.7 to 10.0 MPa and Young’s Modulus from 24.2 to 53.3 MPa. Considerable increment in toughness has been observed as elongation at break improved from 27.5 to 57.2%. This showed enhanced blending between the components. When citric acid content was increased to 5 wt% the tensile strength and modulus increased by 55 and 517%, respectively. At the same time, the elongation-at-break percentage decreased by 44%. FTIR results show cross-linking of PVA and starch molecules with citric acid created –C = C– groups at the cost of –OH groups in PVA as well as starch.

Dai *et al.* [51] reinforced the PVA/CMC hydrogels with graphene oxide and bentonite which could use as proficient adsorbents for methylene blue (MB). This introduction effect was observed by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray diffraction (XRD), thermogravimetry (TG) and differential scanning calorimetric (DSC). It was found that the thermal stability, swelling ability and MB adsorption capacity improved due to the formation of hydrogen bonding. The maximum adsorption capacity was calculated by using the Langmuir isotherm model and found to be 172.14 mg/g at 30 °C which is higher than without introducing f-Gr (83.33 mg/g). Thus, it can be used as an eco-friendly, stable and effective adsorbent for wastewater treatment.

6 Conclusions

After the elaborate study of the literature presented different conclusions have been drawn out and summarized that polyvinyl alcohol (PVA) is a nontoxic and thermoplastic polymer that is completely biodegradable and well know matrix material for green composites. Some literature by researchers on thermal, mechanical, and water absorption of the film were studied, and the conclusion was drawn that PVA shows excellent thermal and mechanical properties due to better interfacial adhesion with reinforcing such as flakes, particles, and fibers because they play important role in the fabrication of composite. PVA-based fiber and particle have gained interest in many application fields. The present work also focused on the effect on the thermal and mechanical on PVA-based composites with particles used as reinforcing material at micro/nano level and different polymer used to prepare PVA-based films. The reviewed literature concludes that the major disadvantage of graphene particles as a filler. It does not have a bandgap (cannot be switched off) is also susceptible to oxidative environments. To overcome this problem many researchers studied the functionalization and activation of graphene with the help of various oxidation acid treatments. Therefore, a review on the effect of acid treatment, functional group addition was studied. Graphene particles were functionalized by nitric acid to increase their distribution in the PVA matrix. The effect of these chemical treatments on graphene was studied with comparative analysis with non-functionalized graphene.

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