Materials Today Communications 16 (2018) 353–363

Contents lists available at ScienceDirect

Materials Today Communications

journal homepage: www.elsevier.com/locate/mtcomm

Biopolymer reinforced nanocomposites: A comprehensive review

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ARTICLE INFO

Keywords:
Biopolymer
Metals
Polymer
Nanocomposite
Nanofiller
Graphene Oxide
Carbonanotube
Silicates

ABSTRACT

Innovation in the field of polymer nanocomposites leads to diverse applications in drug delivery, biosensors, bone regeneration, solar cells, super capacitors etc. A step towards sustainable development, biomimetic approach has been taken into consideration in which vital role is played by the integration of nanofiller in biopolymers. In the present scenario the utilization of biopolymers facilitated by the functionalization of nanofiller by different types of methods which can eradicate agglomeration and enhance thermal, mechanical and electrical properties. This paper reviews the new dimensions in enhancement of properties and their potential applications made by employing a range of metal and carbon based nanofiller into biodegradable polymers in detail. The key factors to incorporate nanofiller are to increase the efficiency of biopolymers due to their high aspect ratio, biocompatibility, low density and high mechanical strength. The observations have been summarized to convey the mechanism and structural changes involved into the biopolymer to the researchers.

1. Introduction

The progression of polymer nanocomposites have blossomed from last few decades due to its outstanding accreditations in structural, electrical, mechanical applications. Inclusion of nanofiller within the polymer host has potential application in biosensors, energy storage devices, photo catalysts, drug delivery etc [1]. Polymer nanocomposites have emerged out to be a paradigm that has exceptional physiochemical properties which is pertinent for the field of modern science. Attributions of nanostructured materials towards miniaturized and smart futuristic technology are the class of materials which are in nanoscale range and disperse into polymer matrix to increase the efficiency that has high aspect ratio and load transfer ability. Polymer nanocomposites were invented by Toyota research group which has bestowed new dimensions by inclusion of organic and inorganic nanofiller owing to the numerous applications [2]. The fabrication of polymer nanocomposite has been facilitated by the use of ultrasonication process for the dispersion of nanofiller, however the controlled amount of weight % and size of the nanomaterial is carefully taken into consideration. The key challenge is to eradicate the agglomerate formation when nanofiller comes into contact with the host polymer. Different methods are adopted to functionalize the surface of nanofiller so that uniform dispersion can be obtained. Today different types of shape i.e. nanotubes, nanofibers, nanoribbons and nanoparticles have come into account to get desired properties [3]. Conventional fillers like carbon black, silicates, calcium carbonates and many more reinforcing agents have also been used on industrial as well as academic scale are being decreased [4]. Several polymers have been extensively studied for e.g. conducting polymers (polyaniline, polypyrrole, polythiophene, polyfuran) which have excellent applications in sensors, fuel and solar cells, EMI shielding and supercapacitors attributed to its high optical and conductive properties [5]. Thermoplastic(polystyrene, polyethylene terephthalate, polycarbonate) and thermosetting polymers (epoxy, polyurethane) based nanocomposites have applications in light emitting diodes [6], dye sensitized solar cells [7], aerospace[8], supercapacitors [9], photo catalyst, energy storage devices and biomedical field[10].

The existing population, global change in climate and industrial pursuit manifests the scientific attention towards the augmentation of biopolymers based nanocomposites. Recent attention has been triggered towards the utilization of different thermoplastic biopolymers and their nanocomposites for the perspective of environmental implications to design novel applications. Biopolymers demand incorporation of nanofiller due to its high production cost and have inadequate characteristics, integration of nanofiller readily enhance the mechanical strength, electrical conductivity, anti-corrosion, thermal properties etc [11,12]. Mostly biopolymers are biodegradable, therefore it has not destructive impact on the environment because they are derived from renewable resources. They have effective applications in coatings, the interfacial interactions via functional groups between the polymer matrix and nanofiller governs the formation of network with enhanced homogeneity in dispersion and the biodegradability component makes it essential prodigy material. Natural and synthetic

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https://doi.org/10.1016/j.mtcomm.2018.07.004
Received 19 March 2018; Received in revised form 4 May 2018; Accepted 9 July 2018
Available online 24 July 2018
2352-4928/

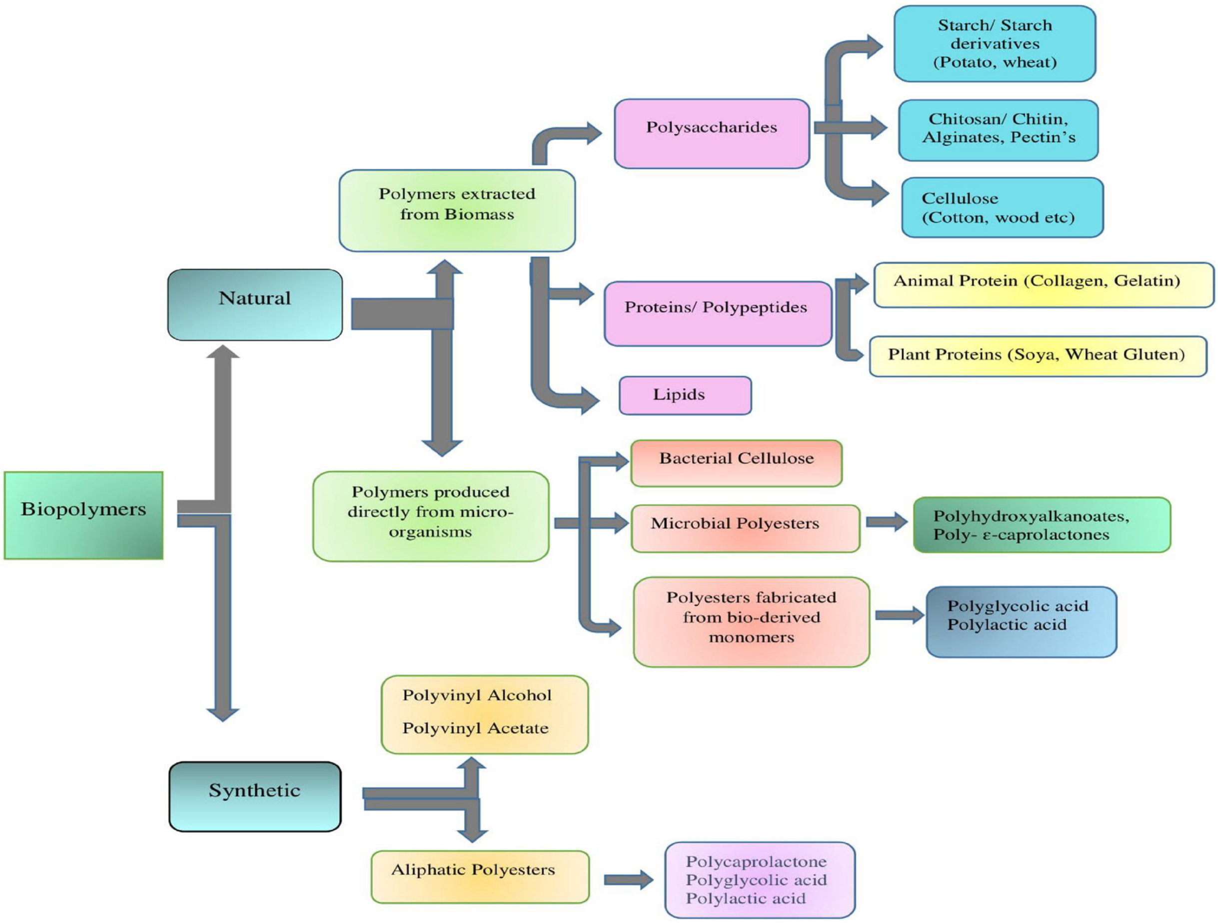

Fig. 1. Depicts the broad classification of Biopolymers [33] (reprint with permission from Rouf and Kokini, 2016).

biopolymers originated from living organisms, polynucleotides, polysaccharides and biomass production which can be a substitute for many other thermoplastics used by incorporating a small amount of nanofiller for e.g. polyethylene, polystyrene etc [13,14].

Fig. 1 depicts the broad classification of biopolymers which include biodegradable and non-degradable thermoplastics. The elaboration in polysaccharides having different functional groups facilitates great dispersion when reinforcing agents are incorporated which have diverse applications. A survey of literature reported the different metal and carbon based nanofillers that has attracted tremendous attention by enhancing properties of the biopolymer matrix. Majority of reviews have classified mainly carbon based nanocomposites in which graphene, carbon nanotubes are immensely studied, where optimization of dispersion is of major concern. Lot of methods need to be explored to get better properties which attribute to the exfoliation of nanofiller into the polymer matrix and also on the cost effective production methods.

Review articles based on the range of polymer nanocomposites which revealed the processing methods, properties, crystallization kinetics and melt rheology have been published [15,16]. Considering the above facts, the focus of this paper is to illuminate the broad classification of processing and applications of metal and carbon based biopolymer nanocomposites. The structural and chemical changes involved in the fabrication and properties of biopolymer nanocomposites have been discussed. The recent progress, current developments and also potential applications of biopolymer nanocomposites are mentioned in this review.

2. Fabrication method involved in biopolymer nanocomposites

Many processing methods have been previously discussed for the synthesis of polymer reinforced nanocomposites which relies on the type of polymer, its molecular weight, solvent to be used and lastly the size of nanofiller which is incorporated [17]. Preparation technique can effectively influence the thermal, electrical and mechanical characteristics of the produced nanocomposite. Unification of polymer nanocomposite requires good homogeneous dispersion of nanofiller as when they come in contact with the matrix they have tendency to form agglomerates, stacking of nanoparticles and incomplete exfoliation [18]. Mainly three techniques involved in the preparation of polymer nanocomposites which are discussed as follows.

2.1. In situ polymerization

This type of polymerization technique usually allows dispersion of nanofiller into the monomer of the polymer matrix used. Polymerization reaction is facilitated by the incorporation of initiator or thermal and photo catalyst [19,20]. It gives effective distribution of nanofiller into matrix compared to other techniques and has easy process but the disadvantage is difficulty in intergallary polymerization and hence limited applications. The diffusion of catalyst is carried out by the inter layer cation exchange [21,22]. Various polymer nanocomposites have been studied by this method for e.g. conducting polymers, polystyrene, polyethylene terephthalates, epoxy etc [23,24].

2.2. Melt intercalation

In melt blending method, no processing solvent is required however dispersion takes place directly in the molten state of thermoplastic polymer via conventional techniques like injection moulding and extrusion [25,26]. Nanofiller and polymer matrix forms intercalated network within polymeric chains to form nanocomposite [27]. Melt mixing of nanofiller and polymer is facilitated by employing shear above the melting point of the host polymer. Mostly polyolefins, polyesters and polylactic acid have been fabricated by this method. This process is not compatible for most of the biopolymers used e.g. PVA (Polyvinyl Alcohol), Polyacrylamide, Chitosan etc [28,29].

2.3. Solution intercalation

For preparation of biopolymer nanocomposites, solution casting technique is the most favorable one which involves simple shear mixing and magnetic stirring of colloidal suspension of nanofiller into the polymer matrix followed by evaporation of solvent in which pre-polymer is added. Suitable solvents can be used e.g. dimethyl formamide, cyclohexanone, acetone, deionized water and ethanol [30,31]. Polymer nanocomposites that have been prepared by this route are Polylactic acid, Polyvinyl chloride, PVA, Polycaprolactone by incorporating a range of nanofiller [32].

3. Biodegradable polymers

Bio based polymers have attracted gigantic consideration as potential substitute of conventional polymers due to its biodegradability and enhanced performance after reinforcement. Fig. 1 shows the broad classification of biopolymers including synthetic and natural polymers. Some of the biopolymers have been discussed in detail.

Polylactic Acid (PLA), is a polymer of lactic acid which is rich in carboxylic functional groups, biocompatible and ecofriendly having good mechanical and optical properties. The disadvantage with PLA is that it has high cost of production and weak performance compared to other polymers. Therefore, it requires reinforcing agents in order to ameliorate its mechanical, thermal and crystallization kinetics. PLA based nanocomposites have phenomenal applications in food packaging, tissue engineering, scaffolds, biomedical devices etc. PLA nanocomposite is easily processable by employing a range of solvents like dimethyl formamide, acetone, chloroform etc but it softens at 60 °C temperature and has low gas barrier and water vapour properties compared to other petroleum based polymers [34].

Chitosan, a derivative of *N*-deacetylated chitin, has received remarkable attention due to its biocompatibility and outstanding antibacterial activities [35,36]. Researchers have been working on to expand its wide area of applications including biosensors, supercapacitors, hydrogels, drug delivery and packaging etc. Its use is limited because it has lower mechanical strength and therefore by incorporating desired reinforcing agents, its properties can be improved because it is biologically renewable.

Cellulose is an industrial biopolymer has broad area of applications in bio absorption, paper packaging, edible coatings etc [37]. It is a derivative of hydroxypropyl methyl cellulose which shows hydrophilic nature. It was reported that it has poor water vapour properties [38], but its nanofiber can increase its tensile strength and young's modulus which has also improved permeability and oxygen barrier properties [39].

Starch has been extensively studied due to its low cost, easily availability, renewability and can be employed in food packaging applications [40]. They have very poor mechanical strength and hence they can combine with a range of nanofiller to improve thermal stability, electrical and mechanical properties. Water resistance can be improved by adding nanomaterials, starch and clay blends have been extensively studied by the scientists which exhibits high strength in edible packaging applications [41]. Significant improvement in tensile strength and young's modulus have also been reported by Cyras *et al* [42].

Alginate, a natural polysaccharidewhich has good fiber properties and can be used in pharmaceuticals, textile manufacturing etc. It is composed of (1,4 linked β-D mannuronic acids and α-L guluronic acid units, derived from cell wall of brown algae and has unique gel forming properties [43]. It is non-toxic and can also be used as biodegradable films. **Poly(vinyl alcohol)**, a water soluble, non-toxic biopolymer has been used in coatings, packaging and has high barrier properties. Due to the presence of hydroxylic group at the edges it can have good interaction with the nanofiller and can be used in bone regeneration, energy storage devices and hydrogels etc [44].

Poly (hydroxy alkanoates) are the class of biopolymers that are renewable and biocompatible having elastomeric characteristics can be fabricated by using solution casting method and which can be used in biosensor and charge dissipating applications [45,46].

Poly ε-caprolactone is a semi-crystalline, synthetic biodegradable polymer in which water is used as a processing solvent. It is highly hydrophilic and easily processable, therefore by addition of nanofiller it can be used in agricultural and biomedical applications [47]. Another form of biopolymers are protein based nanocomposites have been derived from animals and plants that have excellent oxygen barrier and lower vapour properties which can be used in water absorption and food packaging industries [48].

4. Metal based nanocomposites

The purpose of development of technology to generate metal based polymer nanocomposite is to overcome the demerits of polymer matrix to enhance biomedical applications, environmental decontamination, edible packaging applications and many more which has been already reported. The approach to synthesize metal nanoparticles are chemical vapour deposition (CVD), spray pyrolysis, electrodeposition and chemical methods, sol gel process, rapid solidification etc [49,50]. Metal nanoparticles have properties of antibacterial agents, electrical conductivity, optical polarizability and good chemical properties. Metal based nanocomposites undergo reduction in size and functionalization of surface which can also be exploited in plasmonic and sensing applications [51,52]. In last few decades, polymer matrix synthesized by incorporating nanostructured metal reinforcements opened a way to develop an era of bio-organic electronics [53]. Table 1 reports the commonly used metals incorporated in a range of biopolymer matrix elaborating properties and applications of bionanocomposites.

4.1. Methods to fabricate metal and their nanoparticles

There are various methods used to fabricate metals and their oxides as mentioned earlier, we are going to discuss few in detail.

4.1.1. Spray pyrolysis

It is a method in which starting material is added into the processing solvent to get liquid suspension followed by ultrasonication. Carrier gas is purged into the pre-heated beaker, vaporization takes place at elevated temperature which leads to decomposition of oxide material and therefore reduction takes place [54]. This deposition technique is very cost effective and can be used in thin films and coatings.

4.1.2. Sol gel approach and colloidal processing

This chemical method can be carried out very easily involving low temperature, homogeneity and high quality products can be obtained, it is one of the cost effective approach but it gives weak bonding and shows high permeability [55,56]. This method is useful in preparation of metal oxide nanoparticles which requires monomer in colloidal solution to form gel network. This process is also known as wet chemical technique followed by hydrolysis and polycondensation reactions.

4.1.3. Chemical and physical vapour deposition technique

Evaporation of components to give vapour phase followed by saturation in an inert atmosphere to facilitate condensation of metal nanoparticles then thermal treatment is given in inert atmosphere [57,58]. High energy ball milling leads to uniform dispersion and

Table 1
Reports the range of metals and their oxides nanocomposites reinforced with different biopolymer matrix.

Polymer Matrix	Metal (Reinforcing filler)	Processing Method of Nanocomposites	Properties	Applications	Ref
Polyvinyl Alcohol	Silver (Ag)/ Gold (Au)	Solution or In- Situ Intercalation	Enhancement in antibacterial properties, mechanical strength, biomedical devices, and fibers for wound dressing.	Hydrogels, Biosensors, Antibacterial agents, Packaging applications.	[65,66]
	Zinc Oxide (ZnO)		Improvement in thermal stability and photoluminescence property.	Electronic, optical applications, photo electricity and biomedical imaging.	[67,68]
	Titanium Dioxide (TiO_2)		High optical transparency, Self-cleaning property, Coating plastics and cosmetics.	Photocatalytic activity, waste water treatment.	[69,70]
	Iron Oxides		Increase magnetic and electric properties	EMI Shielding applications and energy storage devices	[71,72]
Polylactic Acid	Silver (Ag)/ Gold (Au)	Melt and Solution Intercalation	Good mechanical properties, enhance drug efficacy, vapour sensing.	Surgical implants and tissue culture, Decontamination of polluted soil.	[73,74]
	ZnO		UV Blocking properties, Increased biocidal activity	Potential nano-sized packaging applications.	[75,76]
	TiO_2		UV absorption, catalytic activity, improved surface coatings, self-cleaning property	Light emitting diodes, Bone regeneration scaffolds, biofilms in food contact surface.	[77,78]
	$FeCl_3$		Superparamagnetic behavior	Efficient applications in field of cancer treatment.	[79]
Chitosan, Cellulose	Ag/Au	Solution Casting	Impart surface reactivity, bacterial detection.	Evaluation in cytotoxicity, Biomedical devices.	[80,81]
	ZnO		Antibacterial coating and increased water barrier properties.	Membranes and dyes	[82,83]
	TiO_2		UV resistant, antifungal activity and excellent transparency.	Nanocomposite membranes	[84,85]
	$FeCl_3$		Efficient method to remove heavy metals,	Bio absorbents, Waste water treatment	[86,87]
Alginate, Gelatin, Starch	Ag/Au	Solution Intercalation	Surface stabilizer.	Pharmaceutical industry and food processing.	[88,89]
	ZnO		High thermal stability, strong antimicrobial property.	Food packaging applications.	[90]
	TiO_2		High catalytic efficiency, photochemical stability	Drug delivery systems, biosensors.	

homogeneous mixing in obtaining metal nanoparticles [59]. These process involves sputtering and evaporation.

4.1.4. Electro polymerization

Another way to produce metal matrix based polymer nanocomposite in which monomer precursor in presence of presynthesized metal nanoparticles which leads to formation of polymer network embedded with nanoparticles. It also improves uniform dispersion throughout the surface.

Literature showed that there are two major key points when metal is reinforced into polymer matrix- metal core nanoparticles covered with polymer precursor shell and other is metal and their derivatives embedded into the polymer matrix [60]. Metal nanoparticles and their derivatives are superior chromophores in infrared and visible regions, hence silver, gold and copper nanoparticles show plasmonic band in the visible range of electromagnetic spectrum [61,62]. Biopolymers reinforced with metal and their oxides can be an excellent composite for electrical conductivity, electrolytes in electrochemical systems, optical devices and biosensors [63,64]. Nowadays, *In-situ* method has been opted for the preparation of metal based biopolymer composites based on reduction of metal ions dispersed in polymer matrix or polymerization of monomer dispersed in metal nanoparticles. In this way metal nanoparticles dispersed in biopolymers can be synthesized which has innovative applications having high magnetic and optical properties also mentioned in the Table 1.

5. Carbon based nanocomposites

Polymer nanocomposites emerged out as a new ingenious complex based on layered nanomaterials such as silicates or nanoclay. However, these material exhibits poor electrical and thermal conductivity. In order to improve these shortcomings, carbon based nanofillers have been employed for e.g. carbon black, carbon nanotubes, graphene oxide and its derivatives. Carbon nanomaterials have proved to be an excellent candidate having high surface area, non-corrosive property, light weight and has outstanding mechanical strength and can be used as a good absorbent but due to its high production cost it limits its utilization. Among other nanofiller carbon nanotubes (CNTs) have tendency to form agglomerate within polymer matrix, to eliminate this its surface is treated with functionalizing agent to get homogeneous dispersion. Iijima discovered CNTs that is graphite sheets rolled into tube like form proposed for high strength composites, energy storage devices, biosensors etc [91]. Researchers have reported the ability of load transfer in nanotubes in the same way as non-continuous fibers undergo. Fig. 2 displays the different structural forms of carbon based nanofiller.

Graphene, a sp^2 hybridized, 2-dimension carbon monolayer arranged in a honeycomb lattice fashion proposed by Geim and Novoselov [92]. Graphite followed by exfoliation by ultrasonication can give low yields. To get optimum yield CVD technique has been used for large scale production to generate high quality graphene [93]. Graphene incorporated biopolymer nanocomposites have enormous applications which is beneficial for environment. Several key factors can influence the properties of fabricated polymer nanocomposite which depends on the functional groups present, size of nanoparticle, processing solvent etc. Biopolymers incorporated graphene has provoked its applications in electronic devices, photocatalytic materials, environmental based sensors etc [94]. In contrary to CNTs, graphene and its derivatives have exceptional mechanical and electrical properties which can be attributed to its strong hydrogen bonding interaction

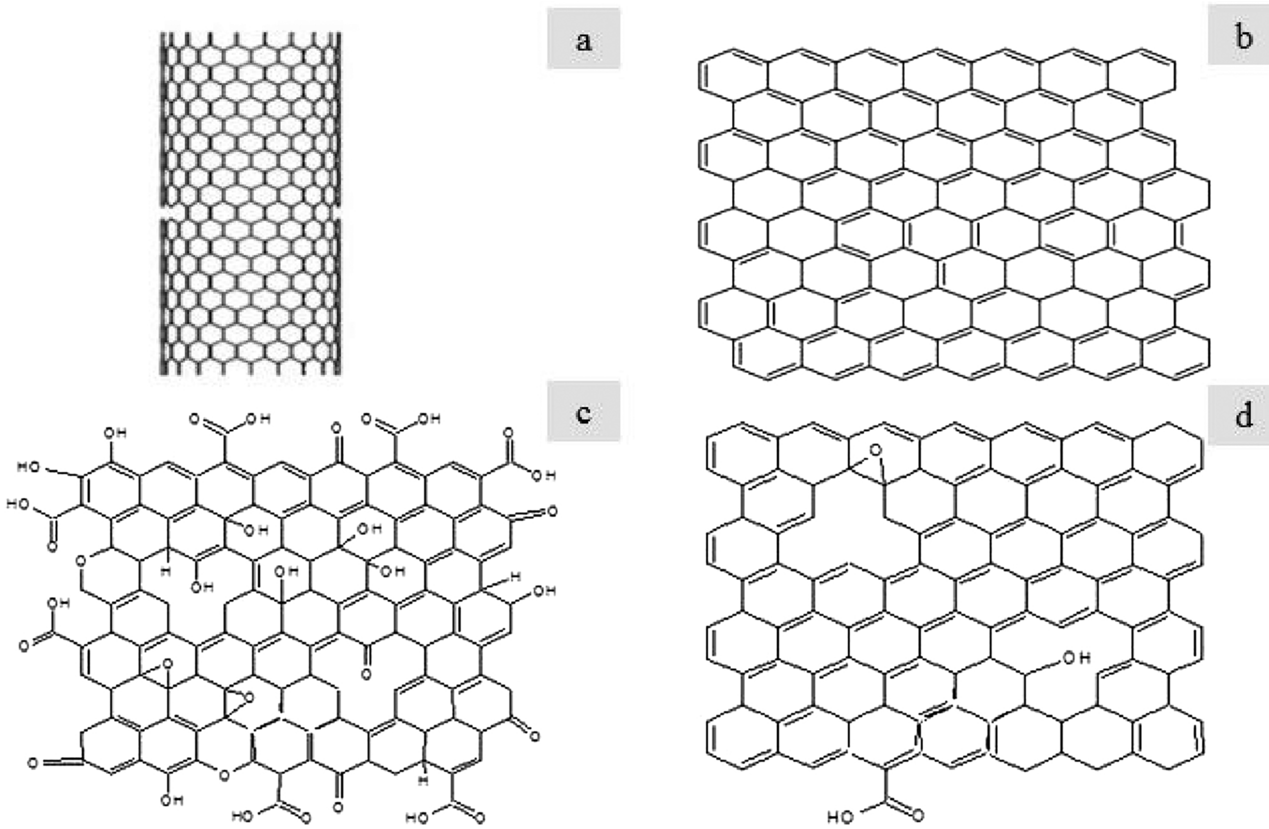

Fig. 2. Displays the structure of different forms of carbon (a) Carbon Nanotube (b) Graphene (c) Graphene Oxide (d) Reduced Graphene Oxide.

amidst functional groups results in high aspect ratio. Graphene and its derivatives can be altered by treating it with different reinforcing agents, such transformation can be done by thermal and chemical reduction and also treating its surface by the range of surfactants so that its reactivity gets increased. Reduction process eliminates oxygen functionalities and can improve the electronic and mechanical properties. However, the performance of the reduced nanomaterial depends on the synergetic effect of functional groups present at the edges and the groups present into the polymer matrix. Compared to CNTs, graphene based nanomaterials has attracted tremendous attention due to its high surface area and extremely high tensile strength.

Table 2 illustrates the overview of different carbon based nanofiller used [95,96].

5.1. Carbon nanotube based biopolymer composite

CNTs are one dimensional carbon materials having aspect ratio higher than 1000 in nanometer range [97,98]. It has poor dispersion in aqueous medium which limits its application in biocompatible materials therefore chemical functionalization of nanotubes are required to eliminate tendency of forming agglomeration. To get full utilization of biobased polymers, it must be compatible with the matrix, latest trends showed that polysaccharides, protein, polypeptides etc can be integrated to get plausible nanocomposite hybrid by incorporating CNTs. CNTs can be classified as single walled CNTs and multi walled CNTs comprised on one or two cylindrical form respectively [99,100]. Unlike conventional polymer nanocomposites, low loading of nanofiller in bio intended applications can modify its properties by enhancing electrical and mechanical properties. PLA being a semi-crystalline biopolymer does not show enhanced crystallinity upon addition of CNT but also immensely effect the electrical conductivity of the host polymer [101]. Kumar *et al* reported the PLA based transducers exhibits strong positive vapour coefficient on addition of 2 and 3% CNT and also showed stable electric signals [102]. PLA-CNTs nanocomposite decreases the surface resistivity but increases the mechanical strength evaluated by Chiu and co-workers [103]. The integration of CNTs in PLA showed reduction in thermal conductivity and increment in electrical conductivity, it is attributed to the electronic circulation in CNT by tunneling where conjunction was separated by polymeric film [104]. Nanocomposite of PLA and CNT amplifies highest change in signal and sensitivity, Fang *et al*

Table 2
Illustrates the properties of carbon based nanofiller and its effect on applications of polymers.

Characteristics	Carbon Nanotube	Graphene	Graphene Oxide	Reduced Graphene Oxide
Synthesis	Chemical Vapour Deposition	Chemical Vapour Deposition Graphite Exfoliation	Oxidation of graphite followed by Exfoliation	Thermal or chemical Reduction of graphene oxide
C: O Ratio	No Oxygen	No Oxygen	2–3	8–246
Young's Modulus (TPa)	1–1.5	1–2	2–4	2–4
Electron Mobility ($cm^2 v^{-1} s^{-1}$)	10,000	10,000–50,000	Insulator	0.05–200
Thermal Conductivity (W/mK)	3500	$4.84–5.30 \times 10^{-3}$	1500 to 5800	0.1–2
Electrical Conductivity (S/m)	3000–4000	7200	$1–5 \times 10^{-5}$	$2–7 \times 10^{-3}$
Production Cost	High	High	Low	Low

also suggested the applications in smart biocomposite product and can also be employed in surface coating [105]. CNT incorporated PLA could controlled photo degradation cycle and can effectively influence the durability of biopolymer, it can also be elucidated that it highly affects the *Tg* (Glass transition Temperature) with an apparent endothermic peak attributed to relax enthalpy. Shih et al revealed that by addition of 4 wt% CNT in PLA, 17.8% increase in storage modulus is observed which can also be useful in covering outer layer of electronic devices. They have also stated that 15.1% enhancement in *Tg* due to high loss modulus [106]. Park *et al* studied the improvement in crystallization through heterogeneous nucleation and decrease in spherulite size of PLA incorporated CNT nanocomposite. They have also examined isothermal behavior through Avrami equation in which significantly improved thermal stability has been reported [107]. It has been also mentioned that nano hybrid of CNT and PLA can efficaciously refine flame retardant and antistatic properties of the biopolymer matrix [108].

Liu and colleagues analyzed that 78% enhancement in tensile strength and efficient load transfer can be seen on addition of 0.8% of functionalized carbon nanotubes [109]. The obtained strength is due to the interfacial interaction between the nanotube and polymer matrix which also affects the mobility of polymeric chain. Loh *et al* investigated that by increasing CNT concentration, strain sensitivity also increases of PVA nanocomposite prepared from layer by layer technique which can be used as corrosive environment sensor [110]. In literature, by integrating CNT in PVA resistivity of nanocomposite decreases and increment in *Tg* is observed by oxidation of CNT, it also decrease melting point [111]. Wang *et al* carried out esterification reaction of PVA reinforced SWCNT and reported enhancement in tack properties at high concentration of nanofiller and also represented high plateau of stress at initial peak [112]. SWCNT-PVA spun nanofibers have tensile strength of 1.5 GPa and 10 S cm^{-1} electrical conductivity at room temperature [113]. SWCNT-PVA electrospun nanofibers showed 1.8 GPa of tensile strength and 80 GPa young's modulus on addition of 60 wt% of SWCNT which was reported by Dalton *et al* [114]. Cheng and co-workers investigated 5500 S cm^{-1} high electrical conductivity and 2088 MPa of tensile strength which can be used in high performance structural applications [115]. Performance of biosensor has been progressed due to reinforcement of CNT in biopolymers, on inclusion of CNT in chitosan electro activity and sensitivity is improved which can be useful in enzymatic biosensors.

Mesquite *et al* reported that utilization of layer by layer technique in fabrication of chitosan-carbon nanowhiskers could magnify the interaction while incorporating high loading of nanofiller and also mentioned the above formation of nanocomposite can be utilized in the field of packaging and biomedical applications [116]. Shokargozar *et al* studied that chitosan and SWNT nanocomposite can be a potential candidate in neural tissue engineering which can also increase the proliferation rate of cell. It has also stated that the fabricated nanocomposite is non-toxic and also showed enhancement in tensile strength [117]. On addition of SWCNT in chitosan influenced the cellular environment to amend osteoblast functions which can be helpful in orthopedic applications [118]. CNT-chitosan nanocomposite can enhance adsorption capability which can be achieved by 0.01 w% CNT and also improved the rate of mass transfer as well as mechanical strength of hydrogel which is reported by Chatterjee *et al* [119]. Cellulose nanocrystals can improve microphase separation of segments among polyurethane matrix and also increase in young's modulus and tensile strength i.e. 344 MPa and 14.86 MPa on incorporation of 30 wt % nanofiller [120]. Cao *et al* also reported the decrease in *Tg* with increasing content of nanofiller.

Starch-MWCNT nanocomposite showed 70% and 35% increment in stiffness and tensile strength at 0.055% loading of nanotubes. Enhancement in impact properties and uniform dispersion of starch by achieving strong adhesion is also reported [121]. Polysaccharides on inclusion of CNTs changes the conformation by increasing sensitivity of chemo-resistive sensors and also radical selectivity of functional groups by specific orientation. Nanocomposite of starch and cellulose nanocrystals functionalized by CNTs represented better biodegradability in contrary to aqueous environments. Blend of Polycaprolactone and MWCNT nanocomposite has given higher input of specific mechanical energy when melt blending employing was carried out and also displayed decrease in residence time in the 25–40% range [122]. Laredo *et al*indicated that PCl/PLA blend incorporated CNT showed improvement in mechanical and electrical properties. They have also demonstrated higher percolation threshold value and well dispersion on CNT in polymeric blend [123]. It has been observed that the synthesis of multifunctional biopolymer nanocomposites by using CNT as a reinforcing agent is attributed to the homogenization of CNTs in matrix, at extremely low content of CNT 34.4% increment in tensile strength is revealed, further it can be used to adhere tissue cells to the substrate [124].

5.2. Graphene oxide and its derivative based biopolymer composite

Graphite can be oxidized by following methods for e.g. Brodie's and hummer's method. Modification of hummer's method leads to shorter duration and high thermal stability of graphene oxide [125,126]. Dispersion of graphene oxide has been carried out by using ultrasonication technique which helps in achieving uniform distribution of smaller fragments of sheets into polar solvent. Graphene oxide is insulating in nature but after its reduction its conductivity gets increased. Many reducing agents have been reported in which hydrazine is very common but due to its toxicity, it can be harmful for biobased applications. Graphene Oxide can also be thermally reduced by keeping it at 1000 °C temperature, low temperature process has also been opted by the researchers. To eradicate this issue, green reducing agents have been explored to functionalize graphene for e.g. alcohol [127], green tea polyphenols [128], amino acid [129], serum albumin [130], bacteria [131], vitamin C [132] etc. Zhu *et al* described the reduction of graphene oxide by using glucose, fructose etc in aqueous ammonia solution [133]. The resulting reduced graphene showed good electro catalytic activity. It has also shortened the reduction duration which attributes the effect of ammonia. Mechanism of resultant nanocomposite of graphene into polymer matrix is governed by hydrophobicity, nature of functional groups, polarity etc.

PLA- Graphene nanosheets were prepared by lypholization using DMF as processing solvent, SEM analysis displayed flat morphology resulted in good interfacial interaction [134]. Pinto *et al* studied the synthesis of PLA-Graphene and used acetone as solvent with 5 h of sonication given for biocompatibility and wettability of the nanocomposites [135]. Mechanical and electrical properties of exfoliated graphene and PLA nanocomposite fabricated by melt blending at 175–200 °C temperature reported by Kim and Jeong [136]. Exfoliation of graphene was carried out by using sulfuric acid. SEM micrographs revealed the homogeneous distribution of exfoliated nanoparticles into the PLA matrix as a result young's modulus and thermal degradation increased on addition of 3 wt% of exfoliated graphene. It is reported that addition of expanded graphite can increase the fire properties of PLA, the resultant nanocomposite passed the charring formation and non-dripping test [137].

The crystallization temperature of nanocomposite decreased at high weight % of GO. PLA based graphene suspension was obtained by freeze drying process in dimethyl formamide solvent. This bionanocomposite was precipitated into methanol and dried. It improved thermal stability of the nanocomposite, also the nucleating effect of expanded graphite and uniform distribution of nanofillers were investigated using Raman and AFM spectra [138]. Pinto *et al* studied the incorporation of graphene nanoplatelets into PLA reduces platelet activation in presence of protein plasma [139]. Contact angle analysis showed presence of GO increases hydrophilicity. Also the polar component increases about 59% with addition of GO. Poly (L-lactic acid) reinforced with GO fabricated *via in-situ* polycondensation of lactic acid monomer through lypholization, it was elucidated that functionalization of GO improved thermal stability and mechanical properties of the resultant nanocomposite. 105% increment in tensile strength is observed on addition of 0.5 wt% of GO compared to neat PLA and displayed little effect on crystallinity [140].

Thin film of PLA reinforced GO nanocomposite was prepared via solvent casting system by comparing plasticized and non-plasticized film, in this permeability decreases towards oxygen and nitrogen. Enhancement in *Tg* is observed on addition of 0.4 wt% of nanofiller [141]. Haibin and co-workers studied cytocompatibilty of PLA-hydroxy appetite incorporated GO nanocomposite prepared via electrospinning process. They observed electrospun fibrous membrane displayed highly rough surface which can be implemented in cell attachment and bone-regeneration applications. The resultant scaffold exhibits better biocompatibility and enhanced mechanical strength which can be an ideal candidate for tissue engineering [142]. Chemically reduced GO via glucose and incorporated into PLA matrix indicated much higher electrical conductivity, on addition of 1.25 vol% of RGO electrical conductivity around 2.2 S/m is achieved due to the chemical and thermal reduction of GO [143].

Liang *et al* worked on fabrication of PVA-GO nanocomposite and reported 76% enhancement in tensile strength and 62% in young's modulus by addition of 0.7 wt%. They have used Halpin Tsai model to predict modulus of nanofiller reinforced composite [144]. Yang and Tao studied layer aligned PVA-GO nanosheets and examined decrease in crystallinity on addition of GO [145]. Chemical reduction of GO *via* hydrazine has been carried out, analysis showed increment in Tg from 76° to 90 °C which is attributed to restriction in mobility of polymeric chain. Moreover SEM micrographs revealed the presence of layered structure of fractured nanocomposite specimen. Covalent functionalization of graphene nanosheets by using amino silane agent incorporated into PVA matrix synthesized by sol gel approach, enhancement in thermal and flame retardant properties were evaluated. However it was reported that addition of 2 wt% of functionalized graphene nanosheets decreases the mass loss rate during the thermal degradation process [146]. Yang and lee investigated the effect of reduced GO on the electrical conductive properties of PVA nanocomposites and mentioned the enhancement in conductivity from 6.04×10^{-3} S/m to 5.92 S/m on addition of 14 wt% of RGO [147]. RGO reinforced PVA sponge has been fabricated for supercapacitor applications, at current density of 0.3 A/g the capacitance value was 200 F/g [148]. By increasing current density, specific capacitance value is decreased, it can be useful in energy storage devices. PVA matrix integrated with RGO showed outstanding enhancement in electrochemical properties compared to GO, 190 F/g capacitance is evaluated in contrary to 13 F/g of PVA-GO nanocomposite [149]. Golafshan *et al* developed a PVA-graphene alginate scaffold by varying different concentration of graphene sheets and observed improved electrical conductivity which is useful in developing the peripheral nerve regeneration device. PVA nanohybrid resulted in reduction in impedance value on addition of 1 wt% of GO and toughness increased by 4 fold used as a thick nerve conduit.

Chitosan based graphene nanofibers were synthesized by electrospinning method to improve the electrical conductivity of suspension. On increasing loading of GO, reduction in porosity and permeability of nanofibrous mats which can be utilized in healing process of wound. *In-vivo* evaluations rate are much higher and efficient in rats. Kamal and Yasin studied the bionanocomposite of chitosan and GO for dye uptake. Brunauer Emmett Teller (BET) test revealed that incorporation of GO nanofiller increased the surface are and absorptive properties of the nanocomposite [150]. This green approach showed high absorption efficacy and can replace petroleum based membranes. It is reported that GO reinforced chitosan nanocomposite showed good resistance against acidic medium [151]. Yang and coworkers fabricated chitosan based graphene nanocomposite by self-assembly approach in aqueous media. They examined well dispersion of GO into chitosan precursor, increment of 122% in tensile strength and 64% of young's modulus on addition of 1 wt% of GO. The *Tg* of nanocomposite increased gradually by the addition of GO component. Glucose biosensor based chitosan GO nanocomposite was produced performed good electrocatalytic activity, it also showed good amperometric response at a range of 2–10 mM and high sensitivity which makes it a desired candidate for electrochemical detection of glucose [152].

In literature, ultraviolet blocking performance has been reported by employing GO-chitosan based nanocomposite fabricated *via* pad dry cure method, it was remarkably enhanced by using chitosan as a dispersant [153]. The ultraviolet transmittance spectra revealed that GO acts as a effective nanofiller to shield UV rays towards cotton fabric. Shamshiri *et al* demonstrated chitosan –GO nanocomposite nanofibrous scaffold exhibited higher drug loading i.e. 98% and controlled release of doxorubicin. The produced nanofibrous scaffold can be useful in treatment of lung cancer [154]. A chitosan reinforced graphene oxide nanocomposite decorated by ZnO can be useful in developing novel antibacterial agents against *E. coli* and *S. aureus* bacteria. It can also be utilized as disinfection agents to inhibit the bacterial growth and high antibacterial activity [155]. Azaranga *et al* observed graphene oxide sheet in gelatin medium is used to inhibit the growth of ZnO nanoparticles on gold [156]. Here, graphene oxide is reduced and the fabricated nanohybrid was used as a photocatalyst to remove methylene blue dye, the efficieny of photocatalyst has been increased by addition of reduced GO. Graphene Oxide nanosheets dispersed in Poly (acrylic acid) and gelatin based hydrogel composite was synthesized which can be used in tissue engineering applications [157]. The results showed that 71% tensile strength and 26% elongation at break are increased by addition of 0.3 wt% GO nanosheets.

Bigi and colleagues analyzed effect of gelatin into collagen reinforced with GO, by adding only 1% of GO into polymer composite more than 50% increment in young's modulus and > 60% in fracture stress was observed [158]. Existence of GO into gelatin films rectified the material stability to buffer solution from 2 days to 2 weeks. The fabrication of silk fibroin incorporated GO nanofiller displayed 145 GPa of tensile modulus which is comparable to stainless steel thin films, by enhancing electrical conductivity, thermal stability and controlled permeability it can be beneficial for bio-nanosensing devices, ion separation, electromagnetic shielding coating etc [159]. Li *et al* reported GO based hydroxyapatite- hyaluronic acid coating using electrophoretic deposition [160]. The results displayed the incorporation of GO increased the deposition rate and inhibit creation of cracks in the nanocomposite coatings. This approach is an efficient method which can be useful in anti-corrosion property on Tin substrate. Bionanocomposite of starch and GO showed enhanced photochemical property and improved thermal and electrical characteristics. Conversion of GO into RGO increases the thermal diffusivity and lower down the electrical resistance of the nanocomposite. Santos and their group developed a chitosan-starch and keratin grafted graphene oxide nanocomposite. The nanohybrid of chitosan and starch exhibited 929% enhancement in storage modulus on addition of 0.5% of GO but on addition of GO in keratin showed decrement in rigidity of the nanocomposite [161]. Polycaprolactone and GO nanocomposite has been prepared through esterification reaction that is chemically reduced, the resulted nanocomposite displayed uniform homogeneity and enhanced electrical conductivity by 14 orders in contrary to neat polymer matrix. *In–vitro* testing showed better biocompatibility and it can be strongly useful in electrically stimulated growth of cells as conducting substrate [162]. Nanofibrous scaffold of GO and Polycaprolactone nanocomposite indicated appreciable cell affinity of GO. The cells exhibited neuron like morphology and mature appearance [163]. It can be an alternative material for biocompatible scaffold in tissue engineering applications.

6. Silicates based nanocomposite

Layered silicates based polymer nanocomposites are first utilized by the researchers at Toyota in Japan, they have used silicates as a nanofiller which can effectively improve mechanical barrier and flame retardant properties [164]. Silicates are one dimensional and natural occurring nanomaterials which are not biodegradable. In last few years polymer clay or polymer layered silicate nanocomposites. The applications of polymer clay nanocomposites in the field of automobile industry, packaging, fuel tanks, electronic and coating industry, coatings etc which is attributed to the efficient mechanical and thermal properties. The research on polymer nanocomposites were discovered to fabricate nanocomposite by using organophilic clay and polyamide 6 (PA 6). Vaia *et al* reported that layered silicates melt mixed with polymers which is in molten state has environmental friendly approach for preparation of nanocomposites by eliminating the use of any solvent [165]. The inclusion of clay as a filler into polymer nanocomposites results in high surface area, large aspect ratio, and microscopic dispersion of filler into the matrix.

The important factors before fabrication of polymer clay nanocomposite are choice of clay and its pretreatment followed by polymer selection. Gonzalez and coworkers examined that addition of 30% Styrene ethylene/butadiene styrene grafted maleic anhydride, toughness gets enhanced and particle size of rubber decreases on addition of maleic anhydride content. Mechanical properties and heat distortion temperature improved but reduction in flammability is observed on comparison to PA6 [166]. Clay is basically a type of layered magnesium, hydrous and aluminum silicates [167]. When clay nanoplatelets dispersed into polymeric matrix, it has aspect ratio around 1000 without breaking. Practically, it has been reported that when mixing is carried out, due to high shear rate it results in 30–300 aspect ratio.

Montmorillonite has large surface area, a hydrous aluminosilicate clay sandwiched in between silicon tetrahedron layers. The thickness of sheet is approximately 1 nm, aspect ratio is 10–1000 and the range of surface area is $750 m^2/g$. Dispersion of layered silicate nanosheets leads to interfacial interaction between the filler and the polymeric material which facilitates stress transfer which results in reduction of weakness of polymer composites. Stacked layers of silicates reinforced polymer nanocomposites generally leads to the gap of van der waal forces of attraction in between the layers. Silicate layers that are modified organically termed as organosilicates or nanoclay. Fig. 3 explains the distinct types of polymer clay nanocomposites. *In-situ* intercalation has been first employed for polyamide-clay nanocomposite then it has been used for other thermoplastics. Exfoliated technique was used for epoxy based clay nanocomposite but the major issue here was removal of solvent. Melt intercalation approach is used mostly for thermoplastic polymer clay nanocomposites in which polymer matrix is mechanically mixed via extrusion or injection moulding conventional techniques at elevated temperature.

The most commonly used approach is melt intercalation. Research by Toyota group observed that nanoclay based nylon 6 nanocomposite can be used in automotive applications for preparation of covers for timing belt. Ube manufactured components of fuel systems and fuel lines which is used for automotive purposes [168]. Hussain and coworkers analyzed the curing mechanism of epoxy reinforced silicate nanocomposite by employing dielectric monitoring technique which can be useful in aerospace applications [169]. The resultant nanocomposite and the technique used can improve parts efficiency, its quality, and mechanical strength, process development. Polymer clay nanocomposites have shown efficient flame retardant properties but the things keep in mind is that it should not release nanosized particles in the atmosphere which can be inhaled by the human and can affect human health. Entirely innovative organo clay should be developed which are biodegradable and has high performance applications in the field of aerospace and automotive.

7. Future challenges and perspectives

In this review, synthesis, properties and applications of biopolymer based on metals and carbonaceous nanofiller composites have been mentioned. A brief of nanoclay based nanocomposites have been also studied in which emission of hazardous materials should be taken care off. Novel fabrication of biodegradable nanocomposite leads to perform smart applications by tailoring its properties. Biomimetic technique has been employed to design bioadsorbents incorporated nanofiller for removal of heavy metals, different types of industrial dye, drug encapsulation, scaffolds, biosensors, supercapacitors etc by enhancing its structural characteristics. Recent research highlighted the potential use of bionanocomposite by opting eco-friendly approach. Among all biobased polymers, PLA and PVA based nanocomposite has been studied extensively which attributes to easy processablity and ecofriendly route. Furthermore, applications in area of proteins and other biopolymers need to be explored. Much attention is needed towards dispersion of nanoparticles into the polymer matrix. The enhancement in properties is a result of interfacial interactions due to the presence of hydroxyl, carboxyl, and amino functional groups present within the polymer matrix and the nanofiller. Biopolymer nanocomposites has

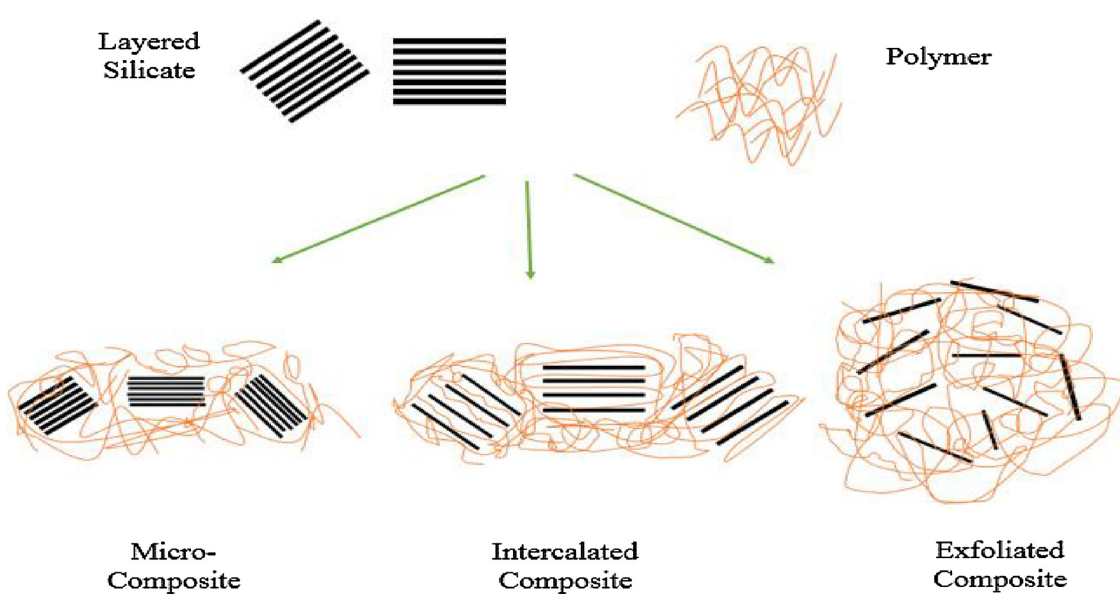

Fig. 3. Types and mechanism of layered silicates reinforced polymer nanocomposites.

been vastly implemented to address the environmental challenges. Nanofillers have tendency to form agglomeration in the polymeric matrix, to overcome this issue chemical modification is required which can integrate distinct functional group moieties which facilitates its homogeneous dispersion so that the resultant nanocomposite can acquire optimal performance. Nanosized metals and their oxides inclusion in biodegradable polymers can open new fortuities in future, lot of travail can be done to explore its properties fully to develop innovative applications. One of the major concern is the reduction of graphene oxide to regain its electrical and mechanical properties, the usage of reducing agent is the greatest challenge. Hence, an eco-friendly and non-toxic approach need to be contemplated. Functionalization of graphene oxide is requisite in order to enhance its electrical, mechanical, thermal properties. Mass production of graphene oxide in large amount has not been achieved yet, hence production of graphene oxide in abundant quantity at relatively low cost should be the prime consideration of the researchers. The main focus in the current strategy should be employing bionanocomposites having no impact on health and environmental implications.

Acknowledgement

Authors would like to thank Netaji Subhas Institute of Technology, University of Delhi, India for financial support.

References

[1] H. Kim, A.A. Abdala, C.W. Macosko, Graphene/polymer nanocomposites, Macromolecules 43 (2010) 65-15.
[2] Pedro Camargo, C. Henrique, Kestur Satyanarayana, Gundappa, Nanocomposites: synthesis, structure, properties and new application opportunities, Mater. Res. 12 (2009) 1–39.
[3] E. Thostenson, C. Li, T. Chou, Review nanocomposites in context, J. Compos. Sci. Technol. 65 (2005) 491–516.
[4] D. Schmidt, D. Shah, E.P. Giannelis, New advances in polymer/layered silicate nanocomposites, Curr. Opin. Solid State Mater. Sci. 6 (3) (2002) 205–212.
[5] Olujinmi M. Folarin, Emmanuel R. Sadiku, Arjun Maity, Polymer-noble metal nanocomposites: review, Int. J. Phys. Sci. 6 (September (21)) (2011) 4869–4882.
[6] G. Eda, Y.Y. Lin, S. Miller, C.W. Chen, W.F. Su, M. Chhowalla, Appl. Phys. Lett. 92 (2008) 233305.
[7] L. Valentini, M. Cardinali, S.B. Bon, D. Bagnis, R. Verdejo, M.A. Lopez Manchado, J.M. Kenny, Use of butylamine modified graphene sheets in polymer solar cells, J. Mater. Chem. 20 (2010) 995–1000.
[8] S.S. Li, K.H. Tu, C.C. Lin, C.W. Chen, M. Chhowalla, Solution-processable graphene oxide as an efficient hole transport layer in polymer solar cells, ACS Nano 4 (2010) 3169–3174.
[9] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, Nature 414 (2001) 359–367, https://doi.org/10.1038/35104644.
[10] L. Chen, G. Chen, L. Lu, Piezoresistive behavior study on fingersensing silicone rubber = graphite nanosheet nanocomposites, Adv. Funct. Mater. 17 (2007) 898–904.
[11] Anju Gupta, William Simmons, Gregory T. Schueneman, Donald Hylton, Eric A. Mintz, Rheological and thermo-mechanical properties of poly(lactic acid)/lignin-coated cellulose nanocrystal composites, ACS Sustainable Chem. Eng. 5 (2017) 1711–1720.
[12] J. Luecha, N. Sozer, J.L. Kokini, Synthesis and properties of corn zein/montmorillonite nanocomposite films, J. Mater. Sci. 45 (2010) 3529–3537, https://doi.org/10.1007/s10853- 010-4395-6.
[13] A.K. Mohanty, et al., Natural Fibers, Biopolymers, and Biocomposites, CRC Press, 2005.
[14] R. Chandra, R. Rustgi, Biodegradable polymers, Prog. Polym. Sci. 23 (1998) 1273 Jump upˆ.
[15] S.S. Ray, M. Bousmina, Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world, Prog. Mater. Sci. 50 (8) (2005) 962–1079.
[16] J.K. Pandey, A.P. Kumar, M. Misra, A.K. Mohanty, L.T. Drzal, R.P. Singh, Recent advances in biodegradable nanocomposites, J. Nanosci. Nanotechnol. 5 (4) (2005) 497–526.
[17] P. Noorunnisa Khanam, Deepalekshmi Ponnamma, M.A. AL-Madeed, Electrical Properties of Graphene Polymer Nanocomposites, Springer Series on Polymer and Composite Materials, DOI 10.1007/978-3-319-13875-6_2.
[18] N. Roy, R. Sengupta, A.K. Bhowmick, Modifications of carbon for polymer composites and nanocomposites, Prog. Polym. Sci. 37 (2012) 781–819.
[19] M. Okamoto, S. Morita, H. Taguchi, Y.H. Kim, T. Kotaka, H. Tateyama, Synthesis and structure of smectic clay/poly(methyl methacrylate) and clay/polystyrene nanocomposites via in situ intercalative polymerization, Polymer 41 (10) (2000) 3887–3890.
[20] M. Okamoto, S. Morita, T. Kotaka, Dispersed structure and ionic conductivity of smectic clay/polymer nanocomposites, Polymer 42 (6) (2001) 2685–2688.
[21] K.J. Yao, M. Song, D.J. Hourston, D.Z. Luo, Polymer/layered clay nanocomposites: 2- polyurethane nanocomposites, Polymer 43 (3) (2002) 1017–1020.
[22] P.B. Messersmith, E.P. Giannelis, Synthesis and characterization of layered silicate-epoxy nanocomposites, Chem. Mater. 6 (10) (1994) 1719–1725.
[23] S.J. Park, M.S. Cho, L.T. Lim, H.J. Choi, M.S. Jhon, Synthesis and dispersion characteristics of multi-walled carbon nanotube composites with poly(methyl methacrylate) prepared by in-situ bulk polymerization, Macromol. Rapid Commun. 24 (18) (2003) 1070–1073.
[24] W.K. Maser, A.M. Benito, M.A. Callejas, T. Seeger, M.T. Martínez, J. Schreiber, et al., Synthesis and characterization of new polyaniline/nanotube composites, Mater. Sci. Eng. 23 (1-2) (2003) 87–91.
[25] S. Kim, I. Do, L.T. Drzal, Thermal stability and dynamic mechanical behavior of exfoliated graphite nanoplatelets-LLDPE nanocomposites, Polym. Compos. 31 (2009) 755–761.
[26] G. Chen, C. Wu, W. Weng, D. Wu, W. Yan, Preparation of polystyrene = graphite nanosheet composites, Polymer 44 (2003) 1781–1784.
[27] W. Weng, G. Chen, D. Wu, Transport properties of electrically conducting nylon 6 = foliated graphite nanocomposites, Polymer 46 (2005) 6250–6257.
[28] M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, A. Okada, Preparation and mechanical properties of polypropylene-clay hybrids, Macromolecules 30 (20) (1997) 6333–6338.
[29] R.A. Vaia, E.P. Giannelis, Polymer melt intercalation in organically modified layered silicates: model predictions and experiment, Macromolecules 30 (25) (1997) 8000–8009.
[30] W.P. Wanga, C.Y. Pana, Preparation and characterization of polystyrene = graphite composite prepared by cationic grafting polymerization, Polymer 45 (2004) 3987–3995.
[31] K. Kalaitzidou, H. Fukushima, L.T. Drzal, A new compounding method for exfoliated graphite-polypropylene nanocomposites with enhanced flexural properties and lower percolation threshold, Compos. Sci. Technol. 67 (2007) 2045–2051.
[32] M. Zammarano, M. Franceschi, S. Bellayer, G.W. Gilman, S. Meriani, Preparation and flame resistance properties of revolutionary self-extinguishing epoxy nanocomposites based on layered double hydroxides, Polymer 46 (2005) 9314–9328.
[33] Tahrima B. Rouf, Jozef L. Kokini, Biodegradable biopolymer–graphene nanocomposites, J. Mater. Sci. 51 (22) (2016) 9915–9945.
[34] J.J. de Vlieger, Green plastics for food packaging, in: R. Ahvenainen (Ed.), Novel Food Packaging Techniques, Woodhead Publishing Limited, England, 2003.
[35] N. Bhattarai, Z. Li, J. Gunn, M. Leung, A. Cooper, D. Edmondson, O. Veiseh, M.-H. Chen, Y. Zhang, R.G. Ellenbogen, M. Zhang, Natural-synthetic poly blend nanofibers for biomedical applications, Adv. Mater. 21 (2009) 2792–2797.
[36] X. Yang, Y. Tu, L. Li, S. Shang, X.-m. Tao, Well-dispersed chitosan/graphene oxide nanocomposites, ACS Appl. Mater. Interfaces 2 (2010) 1707–1713.
[37] G.A. Burdock, Safety assessment of hydroxypropyl methylcellulose as a food ingredient, Food Chem. Toxicol. 45 (12) (2007) 2341–2351.
[38] H.M.C. Azeredo, L.H.C. Mattoso, D. Wood, T.G. Williams, R.J. Avena-Bustillos, T.H. McHugh, Nanocomposite edible films from mango puree reinforced with cellulose nanofibers, J. Food Sci. 74 (5) (2009) N31–N35.
[39] M.R. De Moura, R.J. Avena-Bustillos, T.H. McHugh, J.M. Krochta, L.H.C. Mattoso, Properties of novel hydroxypropyl methylcellulose films containing chitosan nanoparticles, J. Food Sci. 73 (7) (2008) N31–N37.
[40] A. Charles, H.-M. Kao, T.-Ch Huang, Physical investigations of surface membrane–water relationship of intact and gelatinized wheat–starch systems, Carbohydr. Res. 338 (22) (2003) 2403–2408.
[41] H.M. Park, X. Li, C.Z. Jin, C.Y. Park, W.J. Cho, C.S. Ha, Preparation and properties of biodegradable thermoplastic starch/clay hybrids, Macromol. Mater. Eng. 287 (8) (2002) 553–558.
[42] A. Sorrentino, Vittoria V. GorrasiG, Potential perspectives of bionanocomposites for food packaging applications, Trends Food Sci. Technol. 18 (2007) 84–95.
[43] K. Norajit, K.M. Kim, G.H. Ryu, Comparative studies on the characterization and antioxidant properties of biodegradable alginate films containing ginseng extract, J. Food Eng. 98 (2010) 377–384.
[44] I. Cozmuta, M. Blanco, W.A. Goddard Iii, Gas sorption and barrier properties of polymeric membranes from molecular dynamics and Monte Carlo simulations, J. Phys. Chem. B 111 (2007) 3151–3166.
[45] J.S.F. Barrett, A.A. Abdala, F. Srienc, Poly(hydroxyalkanoate) elastomers and their graphene nanocomposites, Macromolecules 47 (2014) 3926–3941, https://doi.org/10.1021/ma500022x.
[46] J. Barrett, Physical and Biochemical Strategies for Improving the Yield and Material Properties of Polyhydroxyalkanoate Biopolymers, (2014).
[47] J. Song, H. Gao, G. Zhu, X. Cao, X. Shi, Y. Wang, The preparation and characterization of polycaprolactone/graphene oxide biocomposite nanofiber scaffolds and their application for directing cell behaviors, Carbon 95 (2015) 1039–1050.
[48] K.S. Miller, J.M. Krochta, Oxygen and aroma barrier properties of edible films: a review, Trends Food Sci Tech 8 (7) (1997) 228–237.
[49] E.S. Yoon, J.S. Lee, S.T. Oh, B.K. Kim, Microstructure and sintering behavior of W–Cu nanocomposite powder produced by thermo-chemical process, Int. J. Refract. Metals Hard Mater. 20 (3) (2002) 201–206.
[50] V. Provenzano, N.P. Louat, M.A. Imam, K. Sadananda, Ultrafine superstrength materials, Nanostruct. Mater. 1 (1) (1992) 89–94.
[51] L. Nicolais, G. Carotenuto, Metal-Polymer Nanocomposites, John Wiley and Sons, Hoboken, NJ, USA, 2005.
[52] F. Faupel, V. Zaporojtchenko, T. Strunskus, M. Elbahr, Metal-polymer nanocomposites for functional applications, Adv. Eng. Mater. 12 (2010) 1177–1190.
[53] M. Muccini, A bright future for organic field-effect transistors, Nat. Mater. 5 (2006) 605–613.
[54] Y.H. Choa, J.K. Yang, B.H. Kim, Y.K. Jeong, J.S. Lee, T. Nakayama, et al., Preparation and characterization of metal: ceramic nanoporous nanocomposite powders, J. Magn. Magn. Mater. 266 (1-2) (2003) 12–19.
[55] R. West, Y. Wang, T. Goodson, Nonlinear absorption properties in novel gold nanostructured topologies, J. Phys. Chem. B 107 (15) (2003) 3419–3426.
[56] P.V. Kamat, M. Flumiani, A. Dawson, Metal-metal and metal-semiconductor

composite nanoclusters, Colloid Surf. A- Physicochem. Eng. Aspects 202 (2-3) (2002) 269–279.
[57] K.L. Choy, Chemical vapour deposition of coatings, Prog. Mater. Sci. 48 (2) (2003) 57–170.
[58] M.C. Joseph, C. Tsotsos, M.A. Baker, P.J. Kench, C. Rebholz, A. Matthews, A. Leyl, Characterisation and tribological evaluation of nitrogen-containing molybdenum-copper pvd metallic nanocomposite films, Surf. Coat. Technol. 190 (2-3) (2005) 345–356.
[59] D.Y. Ying, D.L. Zhang, Processing of Cu–Al2O3 metal matrix nanocomposite materials by using high energy ball milling, Mater. Sci. Eng. 286 (1) (2000) 152–156.
[60] Y.O. Kang, S.H. Choi, A. Gopalan, K.P. Lee, H.D. Kang, Y.S. Song, Tuning of morphplogy of Ag nanoparticles in the Ag/polyaniline nanocomposites prepared by γ-ray irradiation, J. Non-Crystal. Solid 352 (2005) 463–468.
[61] H. Huang, Q. Yuan, X. Yang, Preparation and characterization of metal-chitosan nanocomposites, Colloid Surf. B: Biointerf. 39 (2004) 31–37.
[62] N. Toshima, T. Yonezawa, K. Kushihashi, Polymer-protected palladium-platinum bimetallic clusters: preparation, catalytic properties and structural considerations, J. Chem. Soc. Faraday Trans. 89 (14) (1993) 2537–2543.
[63] K. Suri, S. Annapoorni, R.P. Tandon, N.C. Mehra, Nanocomposite of polypyrrole-iron oxide by simultaneous gelation and polymerization, Synth. Met. 126 (2002) 137–142.
[64] J.H. He, Allomeric scaling law in conductive polymer, Polymer 45 (2004) 9067–9070.
[65] C.M. Santos, J. Mangadlao, F. Ahmed, A. Leon, R.C. Advincula, D.F. Rodrigues, Graphene nanocomposite for biomedical applications: fabrication, antimicrobial and cytotoxic investigations, Nanotechnology 23 (2012) 395101.
[66] A.G. El-Shamy, W. Attia, K.M.A. El-Kader, The optical and mechanicalproperties of PVA-Ag nanocomposite films, J. Alloy Compd. 590 (2014) 309–312; X.D. Cao, C.M. Li, H.F. Bao, Q.L. Bao, H. Dong, Fabrication of strongly fluorescent quantum dot-polymer composite in aqueous solution, Chem. Mater. 19 (2007) 3773–3779.
[67] T.P. Mthethwa, M.J. Moloto, A. De Vries, K.P. Matabola, Properties of electrospun CdS and CdSe filled poly (methyl methacrylate) (PMMA) nanofibres, Mater. Res. Bull. 46 (2011) 569–575.
[68] C. Chen, W. Ma, J. Zhao, Semiconductor-mediated photodegradation of pollutants under visible-light irradiation, Chem. Soc. Rev. 39 (2010) 4206–4219.
[69] Changchao Zhan, Feng Chen, Jintao Yang, Daoxing Dai, Xiaohua Cao, Mingqiang Zhong, Visible light responsive sulfated rare earth doped TiO_2@fumed SiO_2 composites with mesoporosity, enhanced photocatalytic activity for methyl orange degradation, J. Hazard. Mater. 267 (2014) 88–97.
[70] L. Olmedo, P. Hourquebie, F. Jousse, Handbook of Organic 661 Conductive Molecules and Polymers 2 John Wiley & Sons Ltd., 662 Chichester, UK, 1997, p. 663.
[71] Lailesh Kumar, Syed Nasimul Alam, SantoshKumar Sahoo, Mechanical properties, wear behavior and crystallographic texture of Al–multiwalled carbon nanotube composites developed by powder metallurgy route, J. Compos. Mater. 51 (2017) 1099–1117.
[72] M. Gericke, A. Pinches, Biological synthesis of metal nanoparticles, Hydrometallurgy 83 (2006) 132–140.
[73] B. Ankamwar, M. Chaudhary, M. Sastry, Gold Nanotriangles biologically synthesized using tamarind leaf extract and potential application in vapor sensing, Synth. React. Inorg. Met. Nano-Metal Chem. 35 (1) (2005).
[74] R.A. Jain, The manufacturing techniques of various drug loaded biodegradable poly (lactide-co-glycolide) (PLGA) devices, Biomaterials 2 (2000) 2475–2490.
[75] R. Dastjerdi, M. Montazer, A review on the application of inorganic nano-structured materials in the modification of textiles: focus on anti-microbial properties, Colloids Surf. B Biointerfaces 79 (2010) 5e18.
[76] X. Li, Y. Xing, Y. Jiang, Y. Ding, W. Li, Antimicrobial activities of ZnO powder-coated PVC film to inactivate food pathogens, Int. J. Food Sci. Technol. 44 (2009) 2161e2168.
[77] U. Diebold, The surface science of titanium dioxide, Surf. Sci. Rep. 48 (2003) 53.
[78] M. Cho, H. Chung, W. Choi, J. Yoon, Linear correlation between inactivation of E. coli and OH radical concentration in TiO2 photocatalytic disinfection, Water Res. 38 (2004) 1069.
[79] R.D. Baird, S.B. Kaye, Drug resistance reversal – are we getting closer? Eur. J. Cancer 39 (2003) 2450–2461.
[80] A.J. Varma, S.V. Deshpande, J.F. Kennedy, Metal complexation by chitosan and its derivatives: a review, Carbohydr. Polym. 55 (1) (2004) 77–93.
[81] S. Kobayashi, K. Toshitsugu, S.J. Shin-ichiro, Synthesis of artificial chitin: irreversible catalytic behavior of a glycosyl hydrolase through a transition state analogue substrate, Chem. Soc. 118 (1996) 13113–13114.
[82] J.-W. Rhim, S.-I. Hong, H.-M. Park, P.Y.W. Ng, Preparation and characterization of chitosan-based nanocomposite films with antimicrobial activity, J. Agric. Food Chem. 54 (2006) 5814–5822 11.
[83] S. Saravanan, S. Nethala, S. Pattnaik, A. Tripathi, A. Moorthi, N. Selvamurugan, Preparation, characterization and antimicrobial activity of a bio-composite scaffold containing chitosan/nano-hydroxyapatite/nano-silver for bone tissue engineering, Int. J. Biol. Macromol. 49 (2011) 188–193.
[84] D. Archana, J. Dutta, P.K. Dutta, Chitosan–pectin–titanium dioxide nanocomposite film: an investigation for wound healing applications, Asian Chitin J. 6 (2010) 45–46.
[85] X. Li, X. Kong, Z. Zhanga, K. Nana, L.L. Li, X.H. Wang, et al., Cytotoxicity and biocompatibility evaluation of N,O-carboxymethyl chitosan/oxidized alginate hydrogel for drug delivery application, Int. J. Biol. Macromol. 50 (2012) 1299–1305.
[86] M. Akbulut, N.K. Reddy, B. Bechtloff, et al., Flow-induced conformational changes in gelatin structure and colloidal stabilization, Langmuir 24 (2008) 9636–9641.
[87] Y. Tabata, Y. Ikada, Protein release from gelatin matrices, Adv. Drug Deliv. Rev. 31 (1998) 287–301.
[88] J.W. Rhim, Effect of PLA lamination on performance characteristics of agar/ k-carrageenan/clay bio-nanocomposite film, Food Res. Int. 51 (2013) 714e722.
[89] P. Kanmani, J.W. Rhim, Properties and characterization of bionanocomposite films prepared with various biopolymers and ZnO nanoparticles, Carbohydr. Polym. 106 (2014) 190–199.
[90] Ali Nazari, Shadi Riahi, The effects of SnO2 nanoparticles on physical and mechanical properties of high-strength self-compacting concrete, J. Exp. Nanosci. 7 (5) (2012) 559–577, https://doi.org/10.1080/17458080.2010.543991.
[91] K.T. Lau, D. Hui, The revolutionary creation of new advanced materials carbon nanotube composites, Compos. Part B Eng. 33 (2002) 263.
[92] A.K. Geim, K.S. Novoselov, The rise of graphene, Nat. Mater. 6 (2007) 183–191.
[93] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, L. Colombo, R.S. Ruoff, Large-area synthesis of high-quality and uniform graphene films on copper foils, Science 3893 (2009) 1312–1315.
[94] W. Yang, K.R. Ratinac, S.P. Ringer, P. Thordarson, J.J. Gooding, F. Braet, Angew. Carbon nanomaterials in biosensors: should you use nanotubes or graphene? Chem., Int. Ed. 49 (2010) 2114–2138.
[95] G. Zhao, T. Wen, C. Chen, X. Wang, Synthesis of graphene-based nanomaterials and their application in energy-related and environmental-related areas, RSC Adv. 2 (2012) 9286.
[96] T.S. Sreeprasad, V. Berry, How do the electrical properties of graphene change with its functionalization? Small 9 (2013) 341–350.
[97] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene, Science 321 (2008) 385–388.
[98] E.T. Thostenson, Z.F. Ren, T.W. Chou, Advances in the science and technology of CNTs and their composites: a review, Compos. Sci. Technol. 61 (2001) 1899–1912.
[99] M.T. Byrne, Y.K. Gun'ko, Recent advances in research on carbon nanotube-polymer composites, Adv. Mater. 22 (1672) (2010) 1688.
[100] S. Iijima, T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter, Nature 363 (1993) 603–605.
[101] T. Sugai, H. Yoshida, T. Shimada, T. Okazaki, H. Shinohara, New synthesis of high-quality double-walled carbon nanotubes by high temperature pulsed arc discharge, Nano Lett. 3 (2003) 769–773.
[102] K. Kobashi, T. Villmow, T. Andres, P. Pötschke, Liquid sensing of melt-processed poly(lactic acid)/multi-walled carbon nanotube composite films, Sens. Actuators B Chem. 134 (2008) 787–795.
[103] B. Kumar, M. Castro, J.F. Feller, Poly(lactic acid)–multi-wall carbon nanotube conductive biopolymer nanocomposite vapour sensors, Sens. Actuators B Chem. 161 (2012) 621–628, https://doi.org/10.1016/j.snb.2011.10.077.
[104] Wei-Ming Chiu, You-An Chang, Hsan-Yuan Kuo, Meng-Hung Lin, Hua-Chiang Wen, A study of carbon nanotubes/biodegradable plastic polylactic acid composites, J. Appl. Polym. Sci. 108 (2008) 3024–3030.
[105] Z. Antar, J.F. Feller, H. Noël, P. Glouannec, K. Elleuch, Thermoelectric behaviour of melt processed carbon nanotube/graphite/poly(lactic acid) conductive biopolymer nanocomposites, Mater. Lett. 67 (2012) 210–214.
[106] Fang Mai, Youssef Habibi, Jean-Marie Raquez, Philippe Dubois, Jean-Francois Feller, Ton Peijs, Emiliano Bilotti, Poly(lactic acid)/carbon nanotube nanocomposites with integrated degradation sensing, Polymer 54 (2013), https://doi.org/10.1016/j.polymer.2013.10.035 6818e6823.
[107] Yeng-Fong Shih, Yen-Pin Wang, Chi-Fa Hsieh, Preparation and properties of biodegradable PLA/multi-walled carbon nanotubes nanocomposites, Polymer 49 (21) (2008) 4602–4611.
[108] Sang Ho Park, Seung Goo Lee, Seong Hun Kim, Isothermal crystallization behavior and mechanical properties of polylactide/carbon nanotube nanocomposites, Compos. Part A Appl. Sci. Manuf. 46 (2013) 11–18, https://doi.org/10.1016/j.compositesa.2012.10.011.
[109] Luqi Liu, Asa.H. Barber, Shahr Nuriel, H. Daniel Wagner, Mechanical properties of functionalized single walled carbon-nanotube/ polyvinyl alcohol nanocomposites, Adv. Funct. Mater. 15 (2005) 975–980.
[110] Kenneth J. Loh, Junhee Kim, Jerome P. Lynch, Nadine Wong Shi Kam, Nicholas A. Kotov, Multifunctional layer-by-layer carbon nanotube–polyelectrolyte thin films for strain and corrosion sensing, Smart Mater. Struct. 16 (2007) 429–438, https://doi.org/10.1088/0964-1726/16/2/022.
[111] C. Bartholome, P. Miaudet, A. Derré, M. Maugey, O. Roubeau, C. Zakri, P. Poulin, Influence of surface functionalization on the thermal and electrical properties of nanotube-PVA composites, Compos. Sci. Technol. 68 (12) (2009) 2568, https://doi.org/10.1016/j.compscitech.2008.05.021 2009.
[112] Tao Wang, Chun-Hong Lei, Alan B. Dalton, Costantino Creton, Yi Lin, K.A. Shiral Fernando, Ya-Ping Sun, Mihaela Manea, JoséM. Asua, Joseph L. Keddie, Waterborne, nanocomposite pressure-sensitive adhesives with high tack energy, optical transparency, and electrical conductivity, Adv. Mater. 18 (2006) 2730–2734, https://doi.org/10.1002/adma.200601335.
[113] B. Vigolo, P. Poulin, M. Lucas, P. Launois, P. Bernier, Improved structure and properties of single-wall carbon nanotube spun fibers, Appl. Phys. Lett. 81 (2002) 1210.
[114] A.B. Dalton, S. Collins, E. Munoz, J.M. Razal, V.H. Ebron, J.P. Ferraris, J.N. Coleman, B.G. Kim, R.H. Baughman, Super-tough carbon-nanotube fibres, Nature 423 (2003) 703.
[115] Qunfeng Cheng, Jianwen Bao, Jin Gyu Park, Zhiyong Liang, Chuck Zhang, Ben Wang, High mechanical performance composite conductor: multi-walled carbon nanotube Sheet/Bismaleimide nanocomposites, Adv. Funct. Mater. 19 (2009) 3219–3225, https://doi.org/10.1002/adfm.200900663.
[116] Joa˜o P. de Mesquita, Claudio L. Donnici, Fabiano V. Pereira, Biobased nanocomposites from layer-by-layer assembly of cellulose nanowhiskers with chitosan, Biomacromolecules 11 (2010) 473–480, https://doi.org/10.1021/bm9011985.
[117] Mohammad Ali Shokrgozar, Fatemeh Mottaghitalab, Vahid Mottaghitalab, Mehdi Farokhi, Fabrication of porous chitosan/poly(vinyl alcohol) reinforced single-walled carbon nanotube nanocomposites for neural tissue engineering, J. Biomed. Nanotechnol. 7 (2) (2011), https://doi.org/10.1166/jbn.2011.1284.
[118] Owen Im, Jian Li, Mian Wang, Lijie Grace Zhang, Michael Keidar, Biomimetic three-dimensional nanocrystalline hydroxyapatite and magnetically synthesized

single-walled carbon nanotube chitosan nanocomposite for bone regeneration, Int. J. Nanomed. 7 (2012) 2087–2099, https://doi.org/10.2147/IJN.S29743.
[119] Sudipta Chatterjee, Min W. Lee, Seung H. Woo, Adsorption of congo red by chitosan hydrogel beads impregnated with carbon nanotubes, Bioresour. Technol. 101 (2010) 1800–1806, https://doi.org/10.1016/j.biortech.2009.10.051.
[120] Xiaodong Cao, Hua Dong, Chang Mang Li, New nanocomposite materials reinforced with flax cellulose Nanocrystals in waterborne Polyurethane, Biomacromolecules 8 (2007) 899–904.
[121] Lucía M. Famáa, Valeria Pettarinc, N. Silvia, Celina R. Goyanes, Bernal, Starch/multi-walled carbon nanotubes composites with improved mechanical properties, Carbohydr. Polym. 83 (2011) 1226–1231, https://doi.org/10.1016/j.carbpol.2010.09.027.
[122] Tobias Villmow, Bernd Kretzschmar, Petra P¨otschke, Influence of screw configuration, residence time, and specific mechanical energy in twin-screw extrusion of polycaprolactone/multiwalled carbon nanotube composites, Compos. Sci. Technol. 70 (14) (2010) 2045 Elsevier.
[123] E. Laredo, M. Grimau, A. Bello, D.F. Wu, Y.S. Zhang, D.P. Lin, AC conductivity of selectively located carbon nanotubes in poly(ε-caprolactone)/polylactide blend nanocomposites, Biomacromolecules 11 (2010) 1339–13479.
[124] Hae-Hyoung Lee, Ueon Sang Shin, Guang-Zhen Jin, Hae-Won Kim, Highly homogeneous carbon nanotube-polycaprolactone composites with various and controllable concentrations of Ionically-modified-MWCNTs, Bull. Korean Chem. Soc. 32 (1) (2011) 157, https://doi.org/10.5012/bkcs.2011.32.1.157 2011.
[125] B.C. Brodie, On the atomic weight of graphite, Philos. Trans. R. Soc. Lond. 149 (1859) 249–259.
[126] S. William, J.R. Hummers, R.E. Offeman, et al., Preparation of graphitic oxide, J. Am. Chem. Soc. 80 (1958) 1339.
[127] D.R. Dreyer, S. Murali, Y. Zhu, et al., Reduction of graphite oxide using alcohols, J. Mater. Chem. 21 (2011) 3443–3447.
[128] O. Akhavan, M. Kalaee, Z.S. Alavi, et al., Increasing the antioxidant activity of green tea polyphenols in the presence of iron for the reduction of graphene oxide, Carbon 50 (2012) 3015–3025.
[129] J. Gao, F. Liu, Y. Liu, et al., Environment-friendly method to produce graphene that employs vitamin C and amino acid, Chem. Mater. 22 (2010) 2213–2218.
[130] J. Liu, S. Fu, B. Yuan, et al., Toward a universal “adhesive nanosheet” for the assembly of multiple nanoparticles based on a protein-induced reduction/decoration of graphene oxide, J. Am. Chem. Soc. 132 (2010) 7279–7281.
[131] E.C. Salas, Z. Sun, A. Luttge, J.M. Tour, Reduction of graphene oxide via bacterial respiration, ACS Nano 4 (2010) 4852–4856.
[132] J. Lehtola, M. Hakala, K. Hamalainen, Structure of liquid linear alcohols, J. Phys. Chem. B114 (2010) 6426–6436.
[133] C. Zhu, S. Guo, Y. Fang, S. Dong, Reducing sugar: new functional molecules for the green synthesis of graphene nanosheets, ACS Nano 4 (2010) 2429–2437.
[134] Y. Cao, J. Feng, P. Wu, Preparation of organically dispersible graphene nanosheet powders through a lyophilization method and their poly (lactic acid) composites, Carbon 48 (2010) 3834–3839.
[135] A.M. Pinto, S. Moreira, I.C. Gonc¸alves, et al., Biocompatibility of poly (lactic acid) with incorporated graphene- based materials, Colloids Surf. B 104 (2013) 229–238.
[136] I.H. Kim, Y.G. Jeong, Polylactide/exfoliated graphite nanocomposites with enhanced thermal stability, mechanical modulus, and electrical conductivity, J. Polym. Sci. B Polym. Phys. 48 (2010) 850–858.
[137] M. Murariu, A.L. Dechief, L. Bonnaud, Y. Paint, A. Gallos, G. Fontaine, S. Bourbigot, P. Dubois, The production and properties of polylactide composites filled with expanded graphite, Polym. Degrad. Stab. 95 (2010) 889–900.
[138] F. Hassouna, A. Laachachi, D. Chapron, Y. El Mouedden, V. Toniazzo, D. Ruch, Development of new approach based on Raman spectroscopy to study the dispersion of expanded graphite in poly(lactide), Polym. Degrad. Stab. 96 (2011) 2040–2047.
[139] Artur M. Pinto, Susana Moreira, Inês C. Goncalves, Francisco M. Gama, Adélio M. Mendes, Fernão D. Magalhães, Biocompatibility of poly(lactic acid) with incorporated graphene-based materials, Colloids Surf. B Biointerfaces 104 (2013) 229–238, https://doi.org/10.1016/j.colsurfb.2012.12.006.
[140] Wenxiao Li, Xu Zhiwei, Lei Chen, Mingjing Shan, Xu Tian, Caiyun Yang, Hanming Lv, Xiaoming Qian, A facile method to produce graphene oxide-g-poly(L-lactic acid) as an promising reinforcement for PLLA nanocomposites, Chem. Eng. J. 237 (2014) 291–299, https://doi.org/10.1016/j.cej.2013.10.034.
[141] Artur M. Pinto, Joana Cabral, David A. Pacheco Tanaka, Adelio M. Mendes, Fernao D. Magalh˜aes, Effect of incorporation of graphene oxide and graphene nanoplatelets on mechanical and gas permeability properties of poly(lactic acid) films, Polym. Int. (2012), https://doi.org/10.1002/pi.4290.
[142] Hai Bin Ma, Wen Xin Su, Zhi Xin Tai, Dong Fei Sun, Xing Bin Yan, Bin Liu, Qun Ji Xue, Preparation and cytocompatibility of polylactic acid/hydroxyapatite/graphene oxide nanocomposite fibrous membrane, Chin. Sci. Bull. 57 (2012) 3051–3058, https://doi.org/10.1007/s11434-012-5336-3.
[143] Yuxia Shen, Tao Jing, Weijie Ren, Jiewei Zhang, Zhi-Guo Jiang, Zhong-Zhen Yu, Aravind Dasari, Chemical and thermal reduction of graphene oxide and its electrically conductive polylactic acid nanocomposites, Compos. Sci. Technol. 72 (2012) 1430–1435, https://doi.org/10.1016/j.compscitech.2012.05.018.
[144] Jiajie Liang, Yi Huang, Long Zhang, Yan Wang, Yanfeng Ma, Tianyin Guo, Yongsheng Chen, Molecular-level dispersion of graphene into poly(vinyl alcohol) and effective reinforcement of their nanocomposites, Adv. Funct. Mater. 19 (2009) 2297–2302, https://doi.org/10.1002/adfm.200801776.
[145] Xiaoming Yang, LiangLi, SongminShang, Xiao-ming Tao, Synthesis and characterization of layer-aligned poly(vinyl alcohol)/graphene nanocomposites, Polymer (2010), https://doi.org/10.1016/j.polymer.2010.05.034.
[146] Shu-Dong Jiang, Zhi-Man Bai, Gang Tang, Hu Yuan, Lei Song, Fabrication and characterization of graphene oxide-reinforced poly (vinyl alcohol)-based hybrid composites by the sol–gel method, Compos. Sci. Technol. 102 (2014) 51–58, https://doi.org/10.1016/j.compscitech.2014.06.029.
[147] Jian-He Yang, Yu-Der Lee, Highly electrically conductive rGO/PVA composites with a network dispersive nanostructure, J. Mater. Chem. 22 (2012) 8512.
[148] Dongcheol Choi, Kyuwon Kim, Reduced graphene oxide-coated polyvinyl alcohol sponge as a high-performance supercapacitor, Bull. Korean Chem. Soc. (2015), https://doi.org/10.1002/bkcs.10071.
[149] Niyitanga Theophile, Hae Kyung Jeong, Electrochemical properties of poly(vinyl alcohol) and graphene oxide composite for supercapacitor applications, Chem. Phys. Lett. 669 (2017) 125–129, https://doi.org/10.1016/j.cplett.2016.12.029.
[150] Muhammad Arif Kamal, Saira Bibi, Syeda Wishal Bokhari, Ahmad Hassan Siddique, Tariq Yasin, Synthesis and adsorptive characteristics of novel chitosan/graphene oxide nanocomposite for dye uptake, React. Funct. Polym. (2016), https://doi.org/10.1016/j.reactfunctpolym.2016.11.00.
[151] Xiaoming Yang, Yingfeng Tu, Liang Li, Songmin Shang, Xiao-ming Tao, Well-dispersed chitosan/graphene oxide nanocomposites, Appl. Mater. Interfaces 2 (6) (2010) 1707–1713.
[152] Changsheng Shan, Huafeng Yang, Dongxue Han, Qixian Zhang, Ari Ivaska, Li Niu, Graphene/AuNPs/chitosan nanocomposites film for glucose biosensing, Biosens. Bioelectron. 25 (2010) 1070–1074, https://doi.org/10.1016/j.bios.2009.09.024.
[153] Mingwei Tian, Xiaoning Tang, Lijun Qu, Shifeng Zhu, Xiaoqing Guo, Guangting Han, Robust ultraviolet blocking cotton fabric modified with chitosan/graphene nanocomposites, Mater. Lett. 145 (2015) 340–343.
[154] Behnaz Ardeshirzadeh, Nadia Aboutalebi Anaraki, Mohammad Irani, Leila Roshanfekr Rad, Soodeh Shamshiri, Controlled release of doxorubicin from electrospun PEO/chitosan/graphene oxide nanocomposite nanofibrous scaffolds, Mater. Sci. Eng. C 48 (2015) 384–390.
[155] Angshuman Ray Chowdhuri, Satyajit Tripathy, Soumen Chandra, Somenath Roy, Sumanta Kumar Sahu, A ZnO decorated chitosan–graphene oxide nanocomposite shows significantly enhanced antimicrobial activity with ROS generation, RSC Adv. 5 (2015) 49420.
[156] Majid Azaranga, Ahmad Shuhaimia, Ramin Yousefic, A. Moradi Golsheikha, M. Sookhakian, Synthesis and characterization of ZnO NPs/reduced graphene oxide nanocomposite prepared in gelatin medium as highly efficient photo-degradation of MB, Ceram. Int. 40 (2014) 10217–10221.
[157] Shahab Faghihi, Alireza Karimi, Mahsa Jamadi, Rana Imani, Reza Salarian, Graphene oxide/poly (acrylic acid)/gelatin nanocomposite hydrogel: experimental and numerical validation of hyperelastic model, Mater. Sci. Eng. C (2014), https://doi.org/10.1016/j.msec.2014.02.015.
[158] Silvia Panzavolta, Barbara Bracci, Chiara Gualandi, Maria Letizia Focarete, Emanuele Treossi, Konstantinos Kouroupis-Agalou, Katia Rubini, Federico Bosia, Lucas Brely, Nicola M. Pugno, Vincenzo Palermo, Adriana Bigi, Structural reinforcement and failure analysis in composite nanofibers of graphene oxide and gelatin, Carbon (2014), https://doi.org/10.1016/j.carbon.2014.07.040.
[159] Kesong Hu, Maneesh K. Gupta, Dhaval D. Kulkarni, Vladimir V. Tsukruk, Ultra-robust graphene oxide-silk fibroin nanocomposite membranes, Adv. Mater. 25 (2013) 2301–2307.
[160] Ming Li, Qian Liua, Zhaojun Jiaa, Xuchen Xua, Yuying Shi, Yan Chenga, Yufeng Zhenga, Tingfei Xi, Wei Shicheng, Electrophoretic deposition and electrochemical behavior of novel graphene oxide-hyaluronic acid-hydroxyapatite nanocomposite coatings, Appl. Surf. Sci. 284 (2013) 804–810.
[161] Claramaría Rodríguez-Gonzalez, Ana L. Martínez-Hernandez, V.íctor M. Castañ o, Oxana V. Kharissova, Rodney S. Ruoff, Carlos Velasco-Santos, Polysaccharide nanocomposites reinforced with graphene oxide and keratin-grafted graphene oxide, Ind. Eng. Chem. Prod. Res. Dev. 51 (2012) 3619–3629.
[162] S. Sayyar, E. Murray, B.C. Thompson, S. Gambhir, D.L. Officer, G.G. Wallace, Covalently linked biocompatible graphene/polycaprolactone composites for tissue engineering, Carbon 52 (2013) 296–304.
[163] Juqing Song, Huichang Gao, Guanglin Zhu, Xiaodong Cao, Xuetao Shi, Yingjun Wang, The preparation and characterization of polycaprolactone/graphene oxide biocomposite nanofiber scaffolds and their application for directing cell behaviors, Carbon 95 (2015) 1039e1050.
[164] A. Usuki, Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, et al., Synthesis of nylon 6-clay hybrid, Mater. Res. 8 (1993) 1185–1189.
[165] R.A. Vaia, H. Ishii, E.P. Giannelis, Chem. Mater. 5 (1993) 1694–1696.
[166] V. Contreas, M. Cafiero, S. Da Silva, C. Rosales, R. Perera, M. Matos, Polym. Eng. Sci. 46 (2006) 1111–1120.
[167] M.A. Scott, K.A. Carrado, P.K. Dutta (Eds.), Hand Book of Layered Materials, CRC Press book, 2004.
[168] F. Gao, Clay/polymer composites: the story, Mater. Today 7 (11) (2004) 50–55.
[169] K.T. Lau, J. Sankar, D. Hui, Enhancement of the mechanical strength of polymerbased composites using carbon nanotubes, in: M.J. Schulz, A.D. Kelker, M.J. Sunderasen (Eds.), Nanoengineering of Structural, Functional, and Smart Materials, 1st edn., CRC Taylor & Francis, USA, 2006ISBN 0-8-8493-1653-7.