

# A review on the electrical and electrochemical behavior of composites based on carbon nanotube, graphene and their derivatives

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## Abstract

Today, we stand at the edge of exploring carbon nanotube (CNT) and graphene based polymer composites and supercapacitors as next generation multifunctional materials. Supercapacitor materials have been alternative energy source in modern electronics era. Due to their excellent electrical, mechanical and thermal properties, CNTs, graphene and their derivatives have been most promising nanofillers in different fields of applications. In this review, we have focused electrical conductivity of the polymer composites as well as supercapacitor behavior of composites based on CNTs, graphene and their derivatives. To enhance the electrical and supercapacitor properties of the composites, nanofillers are functionalized or chemically modified through different techniques. Here, we have discussed the structure, preparation, electrical and supercapacitor properties of different composites based on CNTs, graphene and their derivatives along with detailed reported scientific literature. Copyright © 2018 VBRI Press.

**Keywords:** Carbon nanotubes, graphene, electrical conductivity, supercapacitor, composites, modification of carbon nanotubes and graphene.

## Introduction

Over the last two decades, conducting polymer composites and supercapacitor materials based on carbon nanofiber, CNTs, and graphene have been attracted in the various fields of applications [1,2]. Among these nanofillers, CNT, graphene and their derivatives have been chosen most promising nanofillers and have huge applications in different fields such as sensors [3], transistors [4], devices [5], catalysts, bioluminescent probes [6], high-performance, and electromagnetic interference (EMI) shielding composites [7]. The electrical conductivity and supercapacitor behavior of the composites strongly depend on the nanofiller concentration, their state of dispersion and nature of the nanofillers. The nature and properties of the CNT and graphene have been discussed below and different chemical modification methods have been used to enhance the properties of the CNT and graphene in the field of conducting polymer composites and supercapacitors materials.

### Carbon nanotubes

CNTs were discovered by Iijima [8] in 1991 and it was the macromolecular analog of fullerenes. After the macroscopic production of C<sub>60</sub>, the progress of CNTs research began quickly and the powder CNTs formed

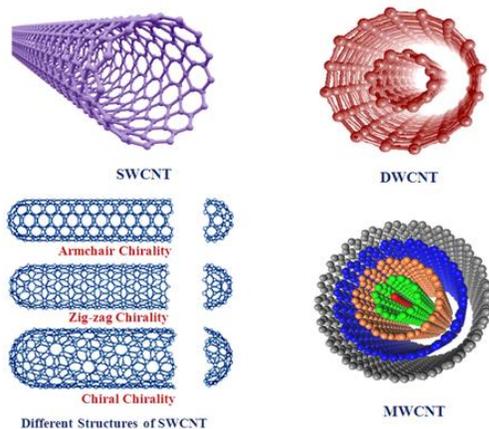
during plasma arc experiments. The different ways are reported for the synthesis of CNTs such as laser ablation [9], high pressure carbon monoxide (HiPCO) [10], arc discharge [11], and chemical vapor deposition (CVD) [12]. The arrangements of CNTs are like carbon hexagons form into tiny tubes. The diameters of the CNTs may lie from a few angstroms to tens of nanometers and lengths are several centimeters. The general view of CNTs is hollow coaxial cylinders which are formed of graphite layers with both ends of the cylinder normally capped by fullerene-like structures. The general phenomena of CNTs is that it is stronger than steel, lighter than aluminum, and more electrically conductive than copper. Depending of the concentric cylinder shells, three types of CNTs are obtained as SWCNTs [11], DWCNTs [13] or MWCNTs [14]. SWCNTs have one concentric cylindrical shells and DWCNT have two concentric cylindrical shells of graphene sheets. However, in the case of MWCNTs, they consists several concentric cylindrical shells of graphene sheets. The structures of CNTs are shown in **Fig. 1**. Thus, observed CNTs are consisting of folded graphene layers with cylindrical hexagonal lattice structure. The theoretical and experimental studies on the cylindrical hexagonal lattice structure of CNTs concluded that this lattice structure is the responsible behind the significantly high thermal, mechanical and electrical properties [15,16] of the CNTs. From the finding of CNTs, it has been

received much attention in the various field due to its exceptionally high mechanical and electrical properties. Due to their excellent electrical properties, CNTs have been much attracted in the different field of potential applications, such as electromechanical actuators [17], composite materials[18], nano-electronic and photovoltaic devices [19], superconductors [20], aerospace, nanowires [21], Li-ion batteries, EMI shielding materials, supercapacitor, actuators, antistatic materials, electro-active materials, pressure sensors, electrostatic discharge (ESD) coatings, percolative conducting polymer composites and as charge-storage capacitors [22,23].

The electrical conductivity of the polymer/CNT composites depends on the dispersion of CNTs in an insulating polymer matrix and proportionally varied with filler concentration. It was well described by percolation theory. The dielectric permittivity and electrical conductivity of the polymer composites are extremely sensitive and they depends on the external parameters such as pressure [24], temperature [25], deformation [26] and alternating current (AC) frequency change [27]. This sensitivity due to external stimuli, electrically conducting polymer composite is highly desirable for sensing applications [28] and frequency sensitive dielectric permittivity can be used for sensing applications and act as an indicator for structure information of different materials [29]. However, stable electrical conductivity of the conducting polymer composite are also important in the various field of applications such as weak dependence of dielectric properties on AC frequency is highly desirable for high-K materials, especially those are suitable for applications in thin films [30]. The frequency dependence of electrical conductivity is a key parameter for EMI shielding, where a high electrical conductivity value is essential at certain frequency values [31].

**Table 1.** Typical properties of CNTs.

Property	SWCNT	MWCNT	DWCNT
Density (g/cc)	~1.3–1.5	~1.8–2.0	~1.5
Electrical conductivity		~10 <sup>2</sup> S/m	~10 <sup>6</sup> S/m
Tensile strength (GPa)	~50–500	~10–60	~23–63
Diameter	~1nm	~20nm	~5nm



**Fig. 1.** Different types of CNTs and different chirality structures of SWCNT.

The electrical conductivity and magnitude of the polymer composites strongly depends on the diameter and chirality of the CNTs. Owing to the excellent mechanical and electrical properties, CNTs have been ideal reinforcing agents for high performance polymer composites. Ajayan et al. [32] first reported CNTs based polymer composites. The research on CNTs based polymer composites have been attracted in the recent scientific area. The number of patents and articles in polymer composite contains CNTs as nanofiller are increasing rapidly every year [1]. For the preparation of polymer composites, different polymer matrices are used including thermoplastics [33,34], liquid crystalline polymers [35,36], thermosetting resins [37,38], conjugated polymers [39], water-soluble polymers [40], among others. The properties of polymer such as tensile modulus [41], tensile strength [42], glass transition temperature [43], morphology, storage modulus, toughness [44], thermal stability, thermal conductivity [45], electrical conductivity [46], supercapacitor behavior, solvent resistance [47], optical properties [48], etc. have been greatly improved due to presence of CNTs in the polymer composites.

Last two decades, several studies have been conducted on CNTs for economical synthesis [49,50], detailed physical/chemical characterization [51,52] due to exploring the potential applications in the various fields [53,54]. The period of nanoscience and nanotechnology flourishes today due to this extensive and modified work on CNTs. However, practical applications of CNTs remain still limited due to its high cost and a lack of effective dispersion. In particular, homogeneous dispersion and distribution of CNTs in the matrices increases the wider applications of CNTs and reduce the cost-effectiveness of materials. CNTs are highly polarizable and smooth-sided materials with an attractive interaction potential of 0.5–2.0 eV per nanometer of tube-to-tube contact in vacuum [55,56]. This very high cohesive force makes CNTs to form bundled structures easily and referred to as ropes [51]. This inherent bundling or entangling nature of CNTs resists the dispersions of CNTs in different solvents or matrices. In fact, the bundled or poorly dispersed CNTs in matrices often play a crucial role in the mechanical performance of a material, which weakens rather than reinforces CNT-based composites. Along with strong cohesive forces, the smooth sidewalls of CNTs, which are composed of a basal layer of carbon atoms, present another performance-limiting factor. The interfacial interactions between matrix and CNTs are very weak and such that CNTs are easily pulled out of a matrix during deformation [43,57]. Thus, functionalization or surface modifications of CNTs have been widely explored to prevent the bundling nature of the CNTs in the matrices. This modification of CNTs increase the dispersion stability and improve the miscibility of CNTs with matrices by enhancing interfacial interactions through chemical bonding [58,59] or physical/mechanical entanglements between the surface-modified CNTs and matrices [1].

Several methods of surface modification have been reported such as covalent bonding of functional groups [60,61], non-covalent wrapping or adsorption of mediating molecules onto the CNT surfaces [62,63] and mechanical grinding [64] to increase the dispersion and distribution of CNTs in solvent media or in polymer matrices.

### Chemical modifications of CNT

To get the high electrical conducting polymer/CNT composites, homogeneous dispersion of CNTs throughout the matrix polymer plays a key role to achieve high value of conductivity at low CNT loading. The homogeneous dispersion of CNT formed a continuous conducting network path in the host polymer which helps to increase the electrical conductivity of the composites. However, the strong Van der Waals force between the CNTs resists the dispersion of CNTs in the matrix polymer. Thus, homogeneous dispersion of CNTs has been a great challenge and several techniques have been used to overcome Van der Waals force among CNTs for better dispersion of CNTs throughout the matrix polymer. The chemical modification or functionalization of CNTs can be an effective method for homogeneous dispersion of CNTs throughout the host polymer. The various methods are reported for the functionalization of CNTs such as defect functionalization, covalent functionalization and non-covalent functionalization [65].

### Defect modifications

The commercially available CNTs are not pure enough. Several impurities such as amorphous carbon or different metal particles are observed in this commercial CNTs. Normally, oxidative methods are extensively used to remove these impurities from commercially available CNTs [66]. Generally, the open ends of CNTs are defected. Due to oxidation of SWCNTs, the purified SWCNTs contain oxidized carbon atoms [67] which present in the form of  $-\text{COOH}$  group. However, the major problem of the oxidative method is that SWCNTs are broken to very small tubes during oxidation [68]. Mawhinney et al. [69] have reported that about 5% of the carbon atoms in the SWCNTs are contained at defective sites when they observed the surface defect site density on SWCNTs by calculating the evolution of  $\text{CO}_2$  (g) and CO (g) on heating to 1273 K. The purified SWCNTs contain about 1-3% acidic sites which was measured by acid base titration method [70]. In spite of this, defect functionalized CNTs are not dispersed thoroughly and to improve the better dispersion, obtained CNTs are modified through covalent attachment of organic groups by converting into acid chlorides and amides [71]. Thus, the obtained organic modified CNTs are homogeneously dispersed and more exfoliated in various organic solvents than the pristine CNTs powder [18].

### Chemical modifications via non-covalent bonding

In general, CNTs are non-covalently functionalized in the presence of surfactants, biomacromolecules or wrapping

with different polymers. Thus, the obtained functionalized CNTs shows better solubility and processability than pristine CNTs. However, physical properties of non-covalently functionalized CNTs do not improve too much. This process involves that CNTs are first dispersed to the aqueous phase in the presence of surfactants [72,73] and hydrophobic part of the micelles covered the CNTs which resulted a strong interaction among them. Thus, this mechanism plays an important role for homogeneous dispersion of CNTs in aqueous medium in the presence of different surfactants such as cationic, anionic and non-ionic surfactants [74-76]. Sodium dodecylbenzene sulfonate (NaDDBS) [77,78] and sodium dodecylsulfate (SDS) [79] are familiar as anionic surfactants. In addition, the dispersion and distribution of CNTs in aqueous solution strongly depend on the nature of the surfactants. The size of the molecule, alkyl or phenyl groups, chain length and accumulated charge of the surfactants greatly affects the interaction between the CNTs and surfactants which varies the dispersion rate of CNTs. In the case of SDS, a weak interaction was observed between SDS and the surface of the CNTs due to the absence of any aromatic group in SDS moiety. So, dispersion of CNT will be less in presence of SDS surfactant. However, a strong interaction was shown in the case of NaDDBS and Triton-X100 due to the existence of electron rich benzene ring in their moiety. The  $\pi$ - $\pi$  interaction between the surface of nanofillers and surfactants enhances the binding and surface coverage which increases the dispersion of the nanofillers significantly [80]. Additionally, among NaDDBS and Triton-X100, NaDDBS will help for more dispersion of CNTs than Triton-X100 due to its large size and longer alkyl chain which facilitate better interaction with nanotube. A schematic representation of the adsorption of surfactants onto the nanotube surfaces are shown in Fig. 2.

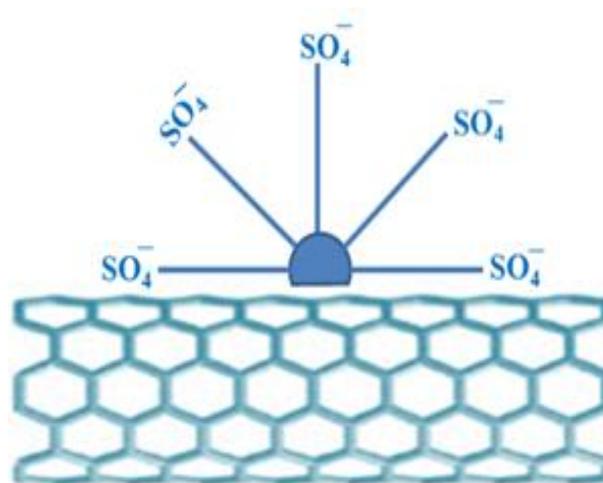


Fig. 2. Schematic representation for the possible adsorption of surfactants onto the nanotube surface [Reproduced with permission from Nano Letters, vol. 3(2), p. 269. Copyright (2003) American Chemical Society (Reference: 76)].

A study already directly carried out about non-surfactant mediated immobilization of protein on CNTs [81] where the hydrophobic regions of the proteins plays a key role for adsorption. Thus, simple and controlled method has been demonstrated for immobilizing proteins onto non-covalently functionalized SWCNTs [82] that involve the nucleophilic substitution of N-hydroxysuccinimide by an amine group on the protein.

The non-covalent functionalization of CNTs can be developed through the interaction between  $\pi$ -electrons of the CNTs and electron rich polymer moiety [82,83] which increases the dispersion of CNTs in different organic [84] or aqueous [85] solvents. Moreover, the physical association among the polymers and CNTs take part a great role to increase the dispersion of the nanofillers in both aqueous [86,87] and organic solvents [88]. The 'wrapping' mechanism [87] is the reason behind this interaction where polymers enfold first CNTs and made supramolecular complexes [89,90]. In these supramolecular complexes, a strong inter- and intramolecular  $\pi$ - $\pi$  interaction observed among electron rich phenyl group of the polymer and  $\pi$  electron cloud surface of the CNTs. Blau et al. [91] prepared polymer/CNT hybrid materials through the suspension of SWCNTs in organic solvents for wrapping the copolymer by nanotubes. Thus, the obtained polymer/CNT hybrid materials show comparatively higher electrical conductivity than the individual components. With the help of this non-covalent method, SWCNT has been modified by incorporating SWCNT within cross-linked and amphiphilic poly(styrene)-block-poly(acrylic acid) copolymer micelles [92]. Thus, prepared encapsulated SWCNT dispersed homogeneously in several of polymer matrices, polar and non-polar solvents. The main drawback of the non-covalent functionalization is the weak interaction between the wrapping molecule and the nanotube which reduces the efficiency of the load transfer of the composite.

### Chemical modifications via covalent bonding

Since, CNTs have delocalized  $\pi$  electrons clouds; they are very reactive and easily formed a covalent bond through different chemical reactions. Thus, the  $sp^2$  carbon atom of CNTs has been changed to  $sp^3$  carbon atoms after chemical reaction for the formation of covalent bond which take part an important role to change their properties such as electronic and transport [93,94]. The major advantage of this functionalization is that the dispersion of the CNTs greatly increased in various solvents and polymers. CNTs can be functionalized through different methods. However, in the most of the cases, CNTs are modified by either modification of carboxylic acid groups of the nanotube surfaces or by direct chemical reactions with nanotubes. For the preparation of  $-COOH$  or  $-OH$  functionalized CNTs, CNTs are mainly oxidized with different methods such as using oxygen, conc. nitric acid, conc. sulfuric acid, mixed acid (mixture of conc. hydrochloric acid and conc. nitric

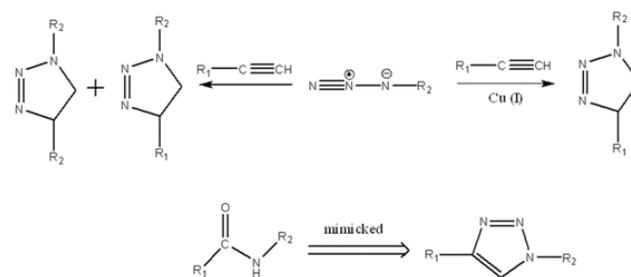
acid) and hydrogen peroxide, etc [95,68]. Thus, the incorporation of acid or hydroxy groups in the CNTs ring create some defects in the C-C bond which indicated some disordered in the lattice structure of CNTs [96,97]. The oxidative modification of CNTs strongly depends on the reaction condition and oxidation rate is influenced by the temperature, time and oxidizing agents during reaction [98]. Since, carboxyl group can easily go to chemical reaction, so, existence of  $-COOH$  groups on the CNT surface will play a crucial role for the modification of CNTs through different organic or inorganic chemical reactions [99,71]. The dithiocarboxylic and thiocarboxylic esters are used for the cross-linking esterification of the CNTs [100]. Thus, functionalization or modifications of CNTs are dispersed homogeneously in various polymers and solvents [93,101]. In addition, the obtained modified CNTs show comparatively higher thermal and mechanical properties than pristine CNTs. The fluorination of CNTs is big challenge and several methods have been considered for the preparation of fluorinated CNTs. Generally, CNTs were fluorinated by passing fluorine gas by changing the temperature of the reaction [102]. This fluorinated CNTs are very reactive and formed different alkylated modified CNTs by the reaction with Grignard reaction. The solubility properties of fluorinated CNTs are high and they form a stable dispersion solution in various solvents such as dimethyl formamide (DMF), chloroform and iso-propanol, etc [103, 104]. Moreover, modifications of CNTs can also be carried out through the chemical reaction with carbenes [105], arylation [106] and nitrenes [107]. Besides the chemical modifications, polymeric modification of CNTs is equally important and it is hugely used for preparation of polymer/CNT composites which has great aspect in the current science and technology [108,109]. Generally, this polymeric modification method of CNTs is familiar as polymer grafting. The "grafting to" and "grafting from" are the two different types of polymeric grafting methods. In the case of the "grafting to" method, the used polymer should have reactive functional group which will go chemical reaction with CNT through covalent bond for the preparation of polymer/CNT nanocomposites. Fu et al. [110] prepared polymer/CNT composites through "grafting to" method. In this study, they have first prepared acylchloride of CNT from carboxylic acid groups of CNTs using thionyl chloride as a chlorine source which easily takes part in the esterification reaction with the hydroxyl groups of dendritic poly (polyethylene glycol) polymer. Qin et al. [111] also studied the polymer/CNT nanocomposites by the "grafting to" method. They have used PS as polymer which has very active azide group in their moiety. This active azide group of polymer goes to cycloaddition reaction for grafting of SWCNTs and forms PS/SWCNT nanocomposites. Thus, several linear polymers such as poly (propionylethylenimine-co-ethylenimine) (PPEI-EI) and poly(vinyl acetate-co-vinyl alcohol) (PVA-VA) have been used for the preparation of polymer grafted CNTs through covalent functionalization by amide linkages or ester

linkages [112,113]. Thus, the solubility property of the prepared PVA/CNT nanocomposites through “grafting to” method was greatly improved and easily soluble in PVA solution. Additionally, the physical properties of the obtained PVA/CNT nanocomposites were also significantly increased after grafting. Several linear polymers have been effectively grafted to CNTs through “grafting to” method for the preparation of polymer/CNT nanocomposites such as PI [114], poly-(2-vinylpyridine) [115], PMMA [116], poly(sodium-4-styrenesulfonate) (PSSS) [117], poly(m-aminobenzene sulfonic acid) [(40)], PPEI-EI [118], dendrimers [119], dendrons [120] and hyperbranched polymers [121], etc. In the current study, the organometallic reagent has been greatly used for preparation of functionalized polymer/CNT nanocomposites [122]. This method involves the reaction of CNT with organometallic n-butyl lithium, followed by covalent bonded with chlorinated polypropylene through coupling reaction. Besides this, the “grafting to” method has little problem which is low content of the grafted polymer because of less active sites on the CNTs [123].

The other polymeric modification method is “grafting from” method where polymer/CNT composites have been prepared by *in-situ* polymerization of monomers in the presence of reactive CNTs. The various *in-situ* polymerization techniques such as cationic, anionic, radical, condensation and ring-opening polymerizations have been considered in the case of “grafting from” method to prepare the very high grafting polymer/CNT which is the major gain of this method. Several polymers are effectively grafted to CNT considering this approach such as PS [124], polyamide 6 [125], PAA [126], PMMA [127], poly(N-isopropylacrylamide) (NIPAM) [128], poly-(tert-butyl acrylate) [129], poly(N-vinylcarbazole) [130] and poly(4-vinylpyridine) [131]. Gao et al. [132] prepared polymer/CNT composites with the help “grafting from” method. This method involves the grafting of functionalized MWNTs with hydrophilic polymer glycerol monomethacrylate (GMA). Zeng et al. [133] covalently grafted poly ( $\epsilon$ -caprolactone) onto CNT surfaces by *in-situ* ring-opening polymerization of  $\epsilon$ -caprolactone in the presence of CNTs using “grafting from” method. Yang et al. [134] prepared soluble MWNTs through amidation reaction of octadecylamine with MWNTs.

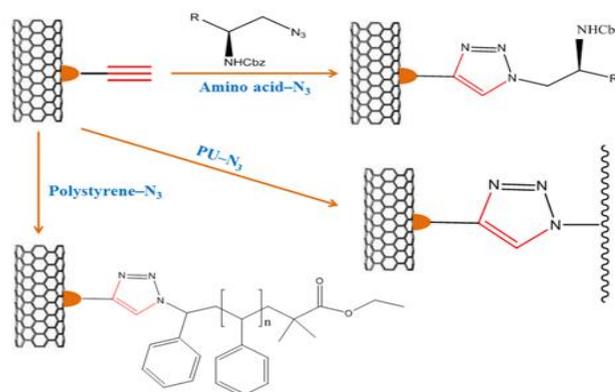
### Chemical modifications through click chemistry

Chemical functionalizations or modifications of the CNTs can also be carried out with the help of click chemistry. The click chemistry is the one of the best methods for the modifications of CNTs through [3+2] dipolar cycloaddition reaction [135]. The small molecules [136] are generally synthesized by this method. In addition, this method is also used for the synthesis of dendronized polymers [137,138], dendrimers [139], and biologically derived macromolecular structures [140].



**Fig. 3.** The coupling of azides and alkynes created triazole linkages in absence and presence of Cu(I) catalyst, the useful topological and electronic feathers with nature's ubiquitous amide connectors [Reproduced with permission from J Am Chem Soc., vol. 126(47), p. 15366, Copyright (2004) American Chemical Society. (Reference: 141)].

The azide and alkyne groups are easily incorporated into polymer chain through this method. The high yield, short reaction time, high purity and region-specificity are the positive side of this method. Additionally, this method is also feasible in aqueous conditions [141]. The highly energetic azides and acetylenes are very much stable and can be used in wide range of reaction conditions. In the case of reaction, the triazole has been considered as a rigid linker that can copy the atom spot in the reaction. The hydrolytic cleavage of the reaction is shown in **Fig. 3**. Recently, many modifications of CNTs through click chemistry are gradually increases and reported related papers are increasing. Thus, click chemistry has been playing a key role for modifications of CNTs in the modern time [45]. **Fig. 4** shows the various click coupling reactions for the modifications of CNTs. Thus, the obtained modified CNTs improved the applications area of the nanofillers and increase the importance of click chemistry.



**Fig. 4.** The attachment of different functionalities on CNTs via click coupling. [Reproduced with permission from Macromolecules vol. 38, p. 8634-48, Copyright (2005) American Chemical Society, (Reference 45)]

### Polymeric modification of carbon nanotubes

The non-covalent and covalent modifications are the main two types of modification methods of CNTs through which a non-covalent or covalent bonding developed among the polymer and CNT, respectively. In the case of non-covalent CNT modification, polymers are covered to the surface of the CNTs. Moreover, a strong possible  $\pi$ - $\pi$

interaction occurred between the electron rich  $\pi$  electrons of CNTs and benzenoid conjugated structure of polymers. The conjugated  $\pi$  electrons system of the CNT is not affected due to these non-covalent modifications which help to keep the physical properties of the composites unchanged.

The other CNT modification method is covalent modification. In this modification method, polymers are linked with CNT by a strong covalent bond. The covalent modification is classified in two categories depending on the nature of the polymer chains such as “grafting to” and “grafting from” method. In the case of “grafting to” approach, the polymer molecules must have reactive groups. The low content of grafted polymer is the major drawback of this approach. Another part of the covalent modification method is “grafting from” method. This method involves *in-situ* polymerization of monomers in the presence of CNTs for the grafting of polymers on the CNT surface. This method is very useful than “grafting to” approach due to high content of grafted polymer is obtained.

#### **Polymeric modification of oxidized carbon nanotubes via ester linkage**

Sun et al. [142] prepared both oxidized SWCNTs and MWCNTs grafted PS copolymer. They have first prepared a solution of poly (styrene-co-p-(4-(4'-vinylphenyl)-3-oxobutanol)) (PSV) in tetrahydrofuran (THF), followed by addition to acyl chloride-activated nanotubes. They have studied the thermogravimetric analysis (TGA) of the composites and shown that approximately 12% and 18% of the CNTs are remain in the PSV-functionalized SWCNT and MWCNT samples after TGA analysis, respectively. Zehua et al. [143] prepared a styrene-maleic anhydride copolymer (SMA) grafted MWCNTs. This SMA-g-CNT was mixed with poly (vinyl chloride) (PVC). Thus, the resultant grafted polymer composites show comparatively higher mechanical and thermal properties. Baskaran et al. [112] prepared PS/MWCNT composites where PS chain contains hydroxyl group and MWCNT contains thionyl chloride group. Riggs et al. [144] prepared poly (vinyl acetate-co-vinyl alcohol) (PVAc-VA) grafted SWCNTs composites through ester linkages where sidewall of the SWCNT is acyl chloride activated. CNTs can be silicon-functionalized and it can be done by ring opening reaction of functionalized polydimethyl siloxanes (PDMS) in the presence of acid modified MWCNTs [145]. The obtained silicon functionalized CNTs are very viscous in nature and almost tar-like at room temperature. Due to this high viscous nature, it can be used in ink-jet printing technology. The polyethylene glycol (PEG) chains were grafted with acyl chloride-activated SWCNT by esterification reaction [146]. At the processing temperature of the polymer, hydroxy-terminated PEG was grafted with acyl chloride activated MWCNT in the absence of solvent [(112)]. Poly (N-vinyl carbazole) copolymer with pendant hydroxyl groups (PVKV) was grafted to oxidized SWCNT through acyl-activation

reaction at vigorous reaction conditions [147]. Wu *et al.* [148] converted the acyl chloride-functionalized MWCNT to hydroxy-modified MWCNT (MWCNT-OH) with hexanediol and bonded to acrylic acid moieties. They have used melt blending method for the preparation of acrylic acid grafted PLLA (PLLA-g-AA). The grafting reaction depends on the reaction condition and higher temperatures and longer reaction times favored the reaction.

#### **Polymeric modification of oxidized carbon nanotubes via amide linkage**

In the composites, amide linkage also plays a crucial role for making bonding between CNT and polymer that create strong interaction among them. Thus, strong physical bonding developed between polymers and CNT which increased the application area of the nanocomposites by increasing its mechanical, thermal and electrical properties. Many researchers have worked and studied the importance of amide linkage in their work. Sun *et al.* [149] discussed about amide linkage in their work where PPEI-EI is grafted with acyl-activated CNTs through amide linkage. Thus, a strong interaction occurred between the polymers with whole nanotube chain. Hu et al. [150] also studied the properties PEI grafted acyl chloride-CNTs and checked the thermal and physical properties in the presence of amide bonding between them. The properties of nonfluorinated polyetherimide in the presence of oxidized MWCNTs have been observed by Ge et al. [114] through solid state reaction which was performed at high temperatures under inert atmosphere in absence of any catalyst. This reaction plays a key role to associate the polymers with CNTs through amide and imide linkages. Qu et al. [151] used amine terminated polyimide for the preparation of nanocomposite in presence of SWCNTs and MWCNTs. Sano et al. [152] have prepared PEO/SWCNT where PEO is monoaminated and SWCNTs are acyl-activated. The microwave radiation has been used for amidation reaction which plays an important role to reduce reaction time for the preparation of nanocomposite [153]. Sun et al. [154] have studied PEO/SWCNT nanocomposite by several methods such as direct thermal heating, acylation-amidation, and carbodiimide-activated coupling. They have used diamine terminated PEO for the preparation of nanocomposite. They reported that direct thermal heating gives the lowest degree of functionalization and carbodiimide activated nanocomposites contained relatively more nanotubes bundles. Haddon *et al.* [155] have used water soluble conducting poly(m-aminobenzene sulfonic acid) (PABS) and functionalized SWCNTs for the preparation of the nanocomposite. The nanocomposites have been prepared through amidation of acyl-activated CNTs with PABS chains.

#### **Background of graphene and their derivatives**

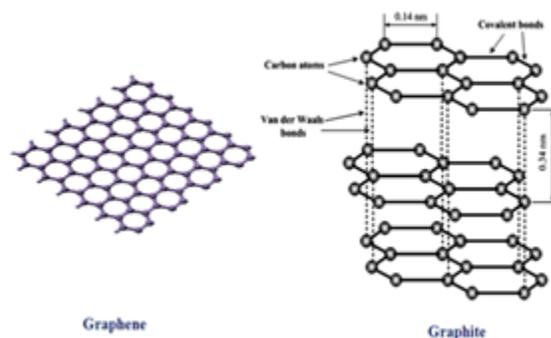
Graphene has been most promising nanofiller in current science. It has  $sp^2$ -hybridized carbon atoms and densely packed in a honeycomb crystal lattice. It is one of the

elements of carbon allotropes including graphite, CNTs, and fullerenes [156,157]. It has been derived from graphite and theoretically established in 1940 [158]. Several groups have been tried to insert the different chemical species or groups between the basal planes of graphite [159,160]. Boehm et al. separated thin lamellae of carbon by heating and chemical reduction of graphite oxide in 1962 [161]. Geim et al. identified successfully single layers of graphene in a simple tabletop experiment in 2004 [162]. Andre Geim and Konstantin Novoselov have been awarded the most prestigious Nobel Prize in Physics 2010 “for ground breaking experiments regarding the two-dimensional material graphene.” This radical discovery of graphene has changed the scientific research in new direction in various fields of research such as chemistry, physics, biotechnology, and materials science. It has exceptionally high electrical conductivity, thermal conductivity, low coefficient of thermal expansion (CTE) behavior [163,164], mechanical flexibility, optical transparency, and thermal properties. These extraordinary and unique characteristics of graphene have been attracted more both in academics and industry. It is a planar monolayer of carbon atoms arranged into a two-dimensional (2D) honeycomb lattice with a carbon-carbon bond length of 0.142 nm [165]. Electrons in graphene behave like massless relativistic particles which contribute to very peculiar properties such as an anomalous quantum hall effect and the absence of localization [166]. It has exceptionally high thermal conductivity ( $5000\text{Wm}^{-1}\text{K}^{-1}$ ) [167], high electron mobility at room temperature ( $250,000\text{cm}^2/\text{Vs}$ ) [168] and superior mechanical properties with Young's modulus of  $1\text{TPa}$  [169].

Now a day, graphene has been most promising nanofillers for the preparation of polymer composites [170,171]. In the presence of graphene, polymer composites show very high electrical conductivity, high mechanical and thermal properties [172,173]. Graphene also plays a crucial role in the fabrication of bio-electronic devices and nano-electronic. Graphene has been better alternative of metal conductors in electronic, electrical devices and electronic circuit material due to its excellent electrical, thermal conductivity and mechanical flexibility. Current research on graphene shows that it has huge applications in flexible displays and touch screens instead of unstable indium tin oxide [174]. It is well established that the superior properties of graphene are associated with its single-layer. However, the fabrication of single-layer graphene is difficult at ambient temperature.

Graphene sheets have high specific surface area and high aspect ratio. They have tendency to form agglomeration in the matrices through  $\pi$ - $\pi$  interaction and van der Waals interactions to each other [175]. This agglomeration of graphene sheets in the matrices increase the cost of the product and pristine graphene sheets are also not suitable in the field of different area. The modification of graphene sheets with hydrophilic or hydrophobic groups increases the dispersion and distribution of graphene sheets in the matrices by strong

polar-polar interactions or by their bulky size [176]. The functionalized graphene sheets easily dispersed in a hydrophilic or hydrophobic media, as well as in the organic polymer. The pristine graphene is not used in the field of nanoelectronic devices, especially for transistor purposes due to the absence of a band gap in pristine graphene. The controlled functionalization of pristine graphene with electron-donating or electron-withdrawing groups (n-doping or p-doping) can be carried out very simply. The molecular level doping of graphene sheets through charge transfer between electron donor and electron acceptor molecules gives rise to significant changes in the electronic structure of graphene. Thus, surface-functionalization and chemical modification of graphene sheets changed the research path in unique direction with various applications in the areas of polymer composites, super-capacitor devices, drug delivery systems, solar cells, memory devices, transistor devices, biosensors etc. **Fig. 5** represents the structure of graphene and graphite.



**Fig. 5.** Graphene is a honeycomb lattice of carbon atoms. Graphite is a stack of graphene layers.

### Chemical functionalization of graphite

Ingenerally, graphite has multilayered structure. The homogeneous dispersion and distribution of graphite layer throughout the matrix polymer plays an efficient role for the application of the polymer composite. Graphite nanoplatelet (GNP) is one kind of graphitic nanofiller which has thickness around in between 0.34 to 100 nm. It has been considered one of the promising carbon based nanofiller for the preparation of conducting polymer composites [177,178] with high thermal and mechanical properties. The structure of graphite is different from silicate clay minerals structure and it does not carry any net charge. Naturally, reactive ion groups do not exist on the graphene layers. Graphite is readily intercalated and can host several molecules, atoms, salts and metal complexes between the expanded graphene sheets (EGS) to make graphite intercalation compounds (GICs). The GNPs are generally prepared from sulfuric acid-intercalated graphite and GO. The modification of graphite provided three different structures of graphite such as GO, EG and GICs. In the current research, graphene has taken as major role in various fields due to its excellent electrical, thermal, mechanical and optical properties.

### Graphene oxide (GO)

Graphene oxide is one of the most promising carbon based nanofillers of graphite and it is water dispersed nanofillers. It has been also known as graphite oxide, graphitic oxide or graphitic acid. It has been prepared by simple method which involved the treatment of graphite flakes with oxidizing agents. In the presence of oxidizing agent, polar groups of the oxidizing agents are penetrated on the surface of graphite which helped to increase the interlayer spacing of the graphene planes [179]. GO is first prepared by Brodie in 1859 where graphite flakes were treated with potassium chlorate and fuming nitric acid [180]. Then, preparation of GO has been modified by Hummers and Offeman. They used simple and easy method for the preparation of GO using anhydrous sulfuric acid, sodium nitrate and potassium permanganate as oxidizing agents with graphite. This method is now considered most promising method for the preparation of GO widely [181]. The epoxy, hydroxyl, carbonyl and carboxyl groups are attached on the graphene sheets in GO structure, as shown in Fig. 6. Unlike graphite, GO is electrically insulating in nature. GO serves as an important intermediate for the preparation of GNPs as discussed later.

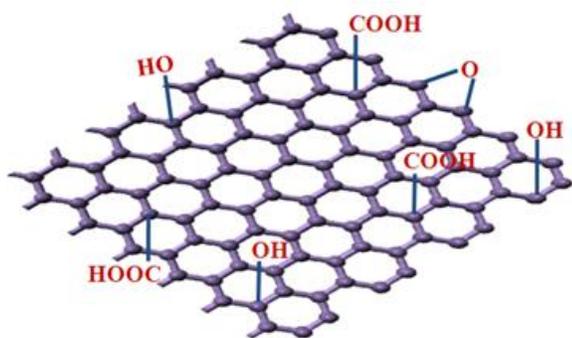
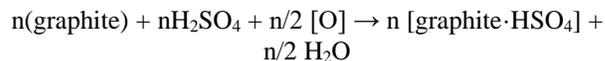


Fig. 6. Representation of the epoxy, hydroxyl, and carboxyl groups in GO.

### Graphite intercalation compounds (GICs)

GICs are one kind of nanofiller of graphite which are prepared through the incorporation of atomic or molecular layers of various chemical species in between the graphite layers [182]. In the case of GICs, the graphene layers either accept electrons from the intercalated species or donate the electrons to the intercalated species. GICs are classified into two categories, one is donor-type GICs and another is acceptor type GICs. For donor-type GICs, graphite layers are intercalated by electron donors like alkali metals (e.g., potassium, sodium, etc.). On the other hand, the intercalation of the graphite layers was done by halogens, halide ions and acids which provided electron for acceptor type GICs. Among the different acids, sulfuric acid, nitric acid, selenic acid and perchloric acid are generally used for the preparation of GICs. GNPs are prepared from GICs and graphite bisulfate is the most commonly used GIC for the preparation of GNPs. A

reaction between graphite and concentrated sulfuric acid can be written by the following equation [183]:



where, O is the oxidant and [graphite. HSO<sub>4</sub>] represents for the GIC. The number of graphite layers among the intercalate layers is recognized as the stage and characteristic ordering property of GICs is the staging phenomenon. The n signifies the stage number. It describes the number of graphene layers that separated adjacent intercalate layers. The stage structure of graphite strongly depends on the intercalation conditions [184]. Shioyama has used unsaturated hydrocarbons for intercalation of graphite and reported that dehydrated isoprene, 1,3-butadiene and styrene could be co-intercalated into the graphite layers of alkali metal-GICs [185]. A schematic diagram for the preparation of donor type GIC was shown in Fig. 7.

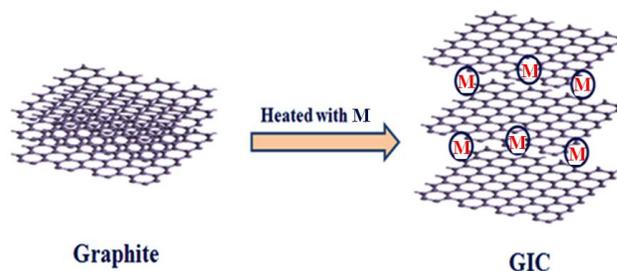


Fig. 7. A schematic diagram for the preparation of donor type GIC.

GICs have played an important role for the preparation of GNPs. Initially, GIC has been prepared by heating of graphite powder in the presence of potassium (K) under vacuum condition, followed by addition of ethanol (EtOH). Then, ethanol reacts with potassium in the reaction chamber which gives potassium ethoxide and evolved hydrogen gas. Thus, the evolution of hydrogen gas from the reaction plays the key role for the preparation of GNPs by the partial exfoliation of the graphitic layers.

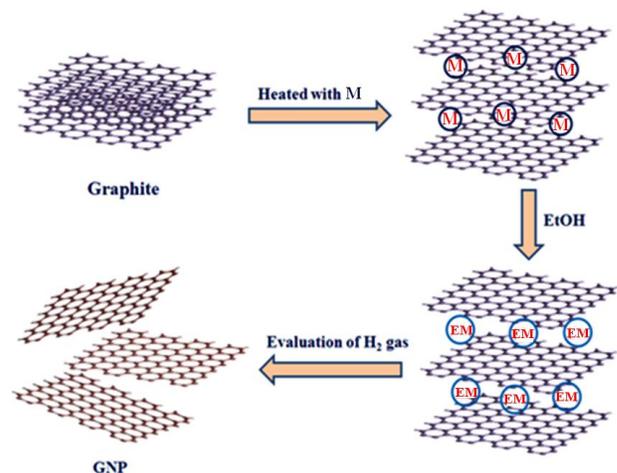


Fig. 8. A schematic representation for preparation of GNPs from graphite powder.

A schematic diagram has been represented for preparation of GNP, as shown in **Fig. 8**. However, this is very tough method for the preparation of GNPs due to the presence of pure alkali metals (like K). This method required moisture free condition and extreme precautions. The GNPs produced by this technique generally have  $40 \pm 15$  graphene layers.

### Expanded Graphite (EG)

Expanded graphite is prepared by heating of GIC at critical temperature or exposed to microwave radiation. In general, graphite bisulfate is used as GIC, although in principle any GIC can be used. Thus, graphite flakes are expanded up to hundred times and formed a vermicular or worm-like structure, known as exfoliated or expanded graphite (EG) [186]. Thus, produced EG has low density and high temperature resistance. EG is composed of nanosheets of 100 to 400 nm [187]. EG has been industrially prepared by very high thermal treatment of graphite flakes with sulfuric acid. EG has good affinity for organic compounds and polymers. Thinner GNPs (~30–80 nm) are obtained by ultra-sonication of EG in different solvents which can be easily dispersed throughout the polymer matrix further by high speed shearing.

### Graphene

Graphene has been considered most promising nanofiller in recent times which has turned scientific research in new direction and hugely demanded in various fields such as nanoelectronics, materials science and condensed matter physics [156,188]. It can be prepared by several methods such as (i) chemical vapor deposition (CVD) of graphite on transition metal surfaces [189], (ii) micromechanical exfoliation of graphite, (iii) epitaxial growth of graphene on electrically insulating substrates like silicon carbide [61]. Among these methods, the methods (ii) and (iii) are not useful for the preparation of large scale graphene. Recently, large amount of graphene and their derivatives (chemically modified graphene, CMG) are synthesized from GO and GICs [190,191]. GO is dispersed easily in water due to the presence of epoxide, hydroxyl groups, carbonyl and carboxyl groups which are chemically reduced with various reducing agents (hydrazine or hydrazine derivatives) and produced conducting graphene sheet. GNPs are combination of multiple graphene sheets which are stacked together. Thus, thickness of GNP is significantly higher than an individual graphene sheet.

On the other hand, large amount of graphene has been prepared by the thermal reduction of GO in the recent time which involved fast heating of GO in inert (nitrogen or argon) atmosphere to get thermally reduced expanded graphene oxide (TRGO) [192]. The fast heating of GO played a crucial role for the exfoliation of the graphene sheets. TRGO is also familiar as functionalized graphene sheets (FGS) with wrinkled sheet structure. The epoxy groups of GO form a network chains through the graphene surface. Due to this wrinkled nature, highly

agglomerated structure was observed. McAllister *et al.* [193] reported that FGS were dispersed homogeneously in different solvents [such as dimethylformamide (DMF), N-methylpyrrolidone (NMP), 1,2-dichlorobenzene (DCB), THF or nitromethane] through ultra-sonication and 80% of the sheets were single layered graphene sheets. FGS is used as most promising carbon nanofiller in polar polymer matrices due to the presence of oxygen functionalities in it. FGS conducts electricity while GO is insulating in nature.

### Surface treatment of graphene via chemical reactions

Pristine graphene are not useful for intercalation by polymer chains. Since, graphene is a bulk material and has tendency to agglomerate in a matrix polymer. Thus, chemical modification of graphene will facilitate to improve better dispersion and distribution of graphene through polymer matrix by preventing agglomeration. The functional groups can be small molecules or polymer chains. The chemical modification of graphene increases the solubility, processability, thermal, electrical and mechanical properties of the graphene which help to improve the better interactions with organic polymers. Different chemical modification of graphene has been carried out such as esterification [194], amination, isocyanate modification [195], electrochemical modification using ionic liquids [196] and polymer wrapping [180] etc. The general methods for the preparation of organo-modified graphene are described as follows.

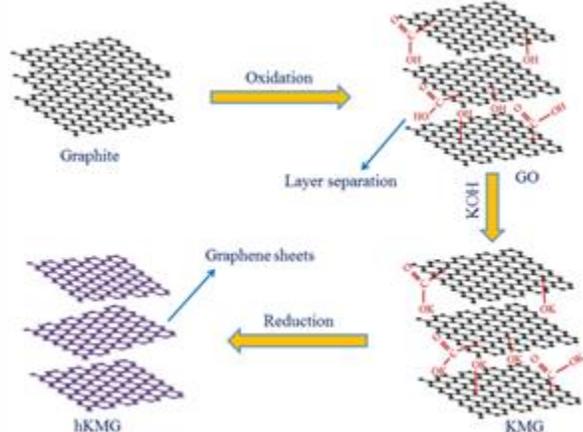
### Functionalization of graphene through chemical reactions

Graphene is chemically modified by the modified Hummers method [197]. In the beginning, graphite oxides are synthesized from graphite powder. Several chemical methods are proposed for the modification of graphene, such as the amidation of the carboxylic groups [198], non-covalent functionalization of reduced graphene oxide [199], nucleophilic substitution to epoxy groups [200], and diazonium salt coupling [201]. The reduction of GO is one of the route for the modification of graphene in a stabilization medium [202].

### Chemical treatment of graphite oxide (GO) via reducing agents

Kuila *et al.* [202] have homogeneously dispersed chemically modified GO in aqueous medium in presence of KOH, as shown in **Fig. 9** [199]. They proposed that negative charge of KOH can react with hydroxyl, epoxy and carboxylic acid groups on the graphene oxide sheets which resulted in extensive coating of the sheets with negative charges and positive charges ( $K^+$  ions). In addition, hydrazine monohydrate was added to KOH-treated graphene oxide and hKMG was obtained in presence of hydrazine hydrate. This suspension solution of hKMG becomes stable for at least 4 months. After that, Li *et al.* prepared stable aqueous colloids of graphene

sheets by electrostatic stabilization of graphite [174]. Thus, many methods have been developed to get better aqueous dispersion of graphene without any surfactant or polymeric stabilizers through simple techniques.

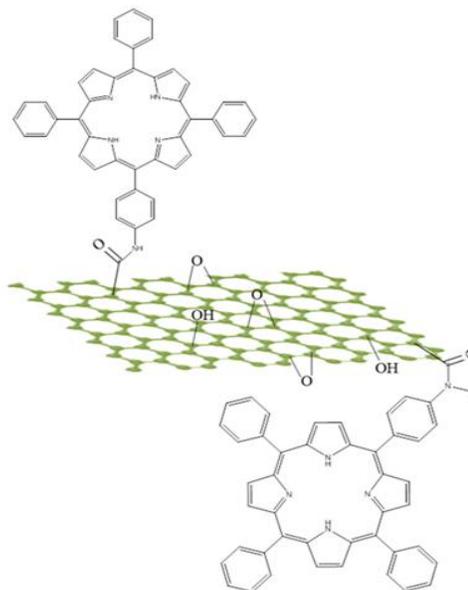


**Fig. 9.** A simple route for the preparation of a homogeneous aqueous suspension of graphene sheets from graphite stack: graphite is oxidized to separate the individual layers of GO. GO is dispersed in water and treated with aqueous KOH solution to obtain KOH modified oxidized graphene (KMG) and finally KMG is reduced using hydrazine to produce hydrazine reduced KOH modified graphene (hKMG) in the form of stable aqueous dispersion of individual graphene sheets. [Reproduced with permission from Prog Polym Sci, vol. 35(11), p. 1350, Copyright (2010) Elsevier, (Reference 199)].

### Covalent functionalization of graphene via chemical treatment

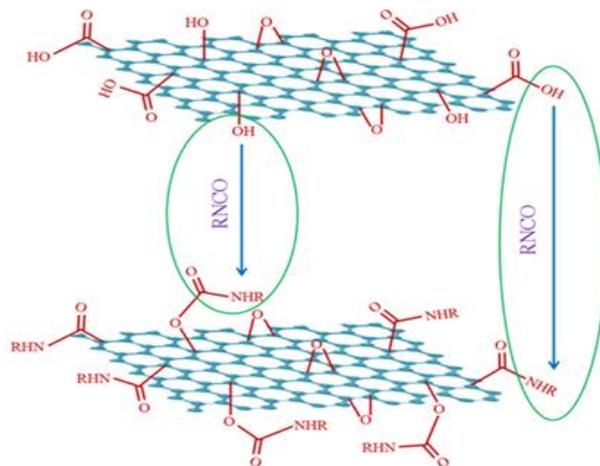
Another method for modification of graphene or graphene oxide is covalent modification technique. Different compounds such as isocyanates, organic amines, alkyl lithium reagents and diisocyanate are used for the modification of graphene or graphene oxide through this modification method [197,203]. The graphene oxide has hydrophilic in nature which is reduced through surface modifying agents. Thus, this modification formed amide and carbamate ester bonds with the carboxyl and hydroxyl groups in GO, respectively. Niyogi et al. [193] reported that an amide coupling reaction occurred between octadecylamine (ODA) and the carboxyl acid groups of graphene oxides. The  $-COOH$  groups of graphene oxide are activated in the presence of thionyl chloride ( $SOCl_2$ ) under reflux conditions. The solubility of ODA-modified GO was  $0.5\text{mg ml}^{-1}$  in THF and it was also soluble in carbon tetrachloride ( $CCl_4$ ) and 1,2-dichloroethane (DCE). Reaction between graphite fluoride and alkyl lithium reagents also increased the solubility of graphene layers [197]. To prepare the functionalized graphene, graphite fluoride reacts with alkyl-lithium reagent in presence of tetra methyl ethylenediamine (TMEDA). Initially, graphite fluoride and TMEDA were dissolved in hexane at  $0^\circ\text{C}$ . Then, alkyl-lithium was added drop wise and kept for 3 days. The covalent attachment of alkyl chains was confirmed by the IR studies [197]. Xu et al. modified the graphene surface using porphyrin ring through the covalent modification [204]. A schematic representation for the modification of graphene sheets

using porphyrin ring through covalent modification, as shown in **Fig. 10**.



**Fig. 10.** Schematic showing the modification of graphene via the covalent attachment of a porphyrin ring on to the GO surfaces. The  $-NH_2$  groups of porphyrin ring are covalently bonded to the carboxyl group of graphene by the amide linkage. Thionyl chloride was used to activate the carboxylic acid group in the presence of porphyrin in DMF. [Reproduced with permission from Advanced Materials, vol. 21(12), p. 1275, Copyright (2009) Wiley-VCH Verlag GmbH, (Reference 204)].

Organic isocyanates react with GO in DMF medium. Then, the reaction mixture was quenched with dichloro methane (DCM) to get modified graphene [194]. In the reaction, isocyanate makes a strong bond with the hydroxyl and carboxyl groups of GO through the formation of carbamate and amide functionalities. Thus, the properties of the GO were increased compared to unmodified GO. The formation of carbamate and amide functionalities between isocyanate and GO was schematically represented in **Fig. 11**.



**Fig. 11.** Schematic showing the modification of GO using organic isocyanate in DMF medium. Scheme shows the reactions of isocyanate group with different functional groups of GO. Isocyanates react with the hydroxyl (left oval) and carboxyl groups (right oval) of graphene oxide sheets to form carbamate and amide functionalities, respectively.

Thus, obtained isocyanate-modified GO forms a stable colloidal dispersion in all polar aprotic solvents such as NMP, DMF, hexamethyl phosphoramide (HMPA) and DMSO. GO was also modified with diisocyanate compounds [203]. The preparation method was similar like isocyanate modification.

### **Non-covalent modification of graphene via chemical treatment**

The stable aqueous dispersion and distribution of exfoliated graphite oxide nanoplatelets aggregates during reduction with hydrazine hydrate [199]. The dispersion of the precipitated materials could not be possible even after a prolonged ultra-sonication in water in the presence of surfactants such as SDS and TRITON X-100. To overcome this difficulty, the reduction of the GO was performed in the presence of polymer/polymeric anions. Thus, a stable dispersion of polymer-grafted graphene was obtained. In this regard, Graphite oxide nanoplatelets was reduced by poly (sodium-4-styrenesulfonate) (PSS) which is an amphiphilic polymer to obtain highly dispersed graphitic nanoplatelets [199]. Xu et al. [205] used water soluble pyrene derivative (1-pyrenebutyrate) for homogeneous dispersion of graphene sheets. The pyrene moiety makes a strong interaction with graphite through  $\pi$ -stacking which plays a key role for better dispersion of graphite [206]. Aqueous dispersion and distribution of reduced exfoliated graphite oxide have already been reported in the presence of sulfonated polyaniline (SPANI) [207].

### **Chemical modification via nucleophilic substitution reaction**

Reaction of amine with GO delivered aliphatic amine modified GO [200]. This is a nucleophilic substitution reaction where lone pair electrons of amine group attack on the epoxy groups of GO [208]. For primary amine,  $C_nH_{2n}+R-NH_2$  ( $n = 2, 4, 8, 12$ ), reaction occurred at room temperature. For long chain aliphatic amines (such as octadecylamine), the reaction mixture was heated under reflux condition for 24 h. Thus, obtained GO derivatives were homogeneously dispersed in different organic solvents. X-ray diffraction (XRD) study confirmed that the interlayer distance of the amine modified GO strongly depends on the lengths of amine chain and their orientation. Bourlinos et al. [200] also reported amino acid modified graphene. They used an alkaline solution of amino acids for the modification of GO.

### **Modification through diazonium salt coupling reaction**

GO was also modified through ary diazonium salts [201]. This is the one of the modification method of GO for homogeneous dispersion of GO in various solvents such as DMAc, NMP and DMF. TGA study confirmed that the diazonium salts modified GO was thermally more stable than neat GO. The epitaxial graphene was chemically modified by the covalent attachment of aryl groups to the basal carbon atoms [209].

### **Electrochemical treatment of graphene for modification**

The electrochemical modification is one of the modification methods of graphene. This method provided colloidal suspension of graphene (CMG) after electrochemical treating of graphite [195]. In this method, a commercial graphite electrode was considered as cathode which was dipped in a phase-separated mixture of water and imidazolium-based ionic liquids followed by applying of constant potential (10–20V) across the electrodes. After 30 min, ionic liquid functionalized graphene (GNPIL) sheets were precipitated from the graphite anode. Thus, obtained GNPIL was homogeneously dispersed in DMF through ultra-sonication. The average width and length of the electrochemically obtained GNPIL were 500 and 700 nm, respectively, confirmed by TEM. The thickness was  $\sim 1.1$  nm, studied by AFM.

### **Modification via $\pi$ - $\pi$ interaction between polymers and graphene**

Surface modification of graphene was also possible by considering the  $\pi$ - $\pi$  interaction between the  $\pi$  orbitals of graphene and  $\pi$  electrons of materials. Liu et al. [210] prepared poly (N-isopropylacrylamide) (PNIPAAm)/graphene composite. Here, a strong  $\pi$ - $\pi$  interaction developed among the  $\pi$  orbitals of graphene and PNIPAAm which plays a crucial role to increase the dispersion of graphene in the composite.

A polymer composite is as a multiphase solid material. Polymer composites are widely applied in the different field of application due to its high performance nature. The homogeneous dispersion of the nanofiller in the composites plays a major role to achieve the better properties of the composites than matrix polymer. Graphene has been considered most promising nanofiller due to its exceptionally high electrical, thermal and mechanical properties for the development of high performance composites.

### **Conducting polymer composites**

Last two decades, conducting polymer composites have taken major role in the various fields such as sensors, transistors, devices, catalysts, bioluminescent probes, high-performance, supercapacitor and EMI shielding. Different conducting nanofillers are used for the preparation of conducting polymer composites such as carbon black, carbon nanofibres, carbon nanohornes, CNT and graphene. CNTs and graphene have been considered among these nanofillers for their high thermal, mechanical and exceptionally high electrical properties. In addition, the surface area and aspect ratio of CNTs and graphene are very high. The conductivity property of the composites not only depended on the concentration of the nanofillers but also their dispersion throughout the polymer matrix. Besides this, processing techniques and nature of the polymers also play a crucial role to get conductivity of the composites. In the conducting polymer

composites, nanofillers form a conductive interconnected network path throughout the host polymer above the percolation threshold of the composites. The percolation threshold ( $p_c$ ) is the point where electrical conductivity of the polymer composite rapidly increased in presence of minimum concentration of nanofiller. The spiderweb like interconnected conducting network structure of the nanofillers plays a crucial role for the conduction of electricity throughout the composites. Both theoretically and experimentally explained the percolation theory. DC electrical conductivity of the polymer composites near the percolation threshold can be explained with the help of following power law equation.

$$\sigma_{DC}(p) = \sigma_0(p - p_c)^t \quad \text{For } p > p_c$$

where,  $t$  denoted the critical exponent. Many researchers [211,212] studied that different polymer composite systems have different critical exponent ( $t$ ) values. The values of  $t$  also show different for 2D and 3D lattices on the basis of theoretical calculations. In general, the calculative ' $t$ ' values will exist in the region from 1.10 to 1.43 for 2D lattice and lower than 2.02 for 3D lattice.

The reported values of percolation threshold are observed in the region from 0.0025 wt% [213] to several wt% [214]. The aspect ratio, alignment, dispersion, degree of surface modification of nanofillers, nature of the polymer and processing techniques seriously effect on the percolation threshold [96,215]. The homogeneous dispersion of the nanofillers decreased the percolation threshold value. The percolation threshold of epoxy/CNT composites is reduced in the presence of palmitic acid compared to the composites without palmitic acid. Presence of palmitic acid plays a crucial role for the efficient dispersion of CNTs in the epoxy matrix which help to reduce percolation value [176]. The aligned CNTs are more effective than entangled nanotubes for the preparation of electrically conductive polymer composites [291] due to better dispersion of aligned CNTs in the polymer matrix. Thus, obtained electrical conductivity of SWCNT/epoxy composites with aligned SWCNTs was more than that of SWCNT/epoxy composites without aligned SWCNTs [216]. The percolation threshold of the polymer composites was greatly influenced on the aspect ratio of the nanofillers. Due to high surface area and nano-sized of the nanofillers, they are homogeneously dispersed throughout the matrix polymer than macrofillers and tremendously reduced the percolation threshold.

The chemical functionalization of nanofillers disrupted the extended  $\pi$ -conjugation and shows low electrical conductivity than untreated nanofillers [217]. Cho et al. [97] reported that electrical conductivity of the surface-modified MWCNT is less than unmodified MWCNT. This is attributed that the defects are increased in the lattice structure of C-C bond on the surface of the nanotubes after acid modification. Thus, modification of the nanofillers significantly reduced the electrical conductivity in several cases. Many researchers studied

that the electrical conductivity of the polymer composites improved after chemical modification of the nanofillers. Tamburri et al. [218] reported that -COOH and -OH modified SWCNTs shows higher electrical conductivity than that of untreated SWCNTs.

### Percolation threshold

In general, the interaction was observed at molecular level between nanofillers and polymer in composite. This interaction affected the properties of the polymer. This is known as percolation threshold where the minimum concentration of nanofillers required forming a cluster through the whole composite system. Surprisingly, the formation of percolating clusters and its control over the formation in the composites is still not well understood. This would provide opportunities to manipulate the percolation threshold and the level of conductivity to produce a composite with an optimized conductivity at minimum loading of nanofillers. For the preparation of conducting polymer composites, various types of conducting nanofillers can be used. However, preparation of low cost composite will be industrially more preferable. For this reason, minimizing the experimental percolation threshold with high the mechanical characteristics is very much important. At present, it seems that the physics of electrically conducting networks of nanofillers throughout the polymer is not well described. Various studies have been proposed by both numerically and analytically on percolation to obtain maximum electrical conductivity at minimum nanofiller loading. It has been now more challenging to decouple the effect of nanofiller size and their dispersion on the percolation. Hence, the effect of the nanofiller size on percolation has not been well established due to dispersion of the nanofillers in composites cannot be assured. In general, nanofillers are typically used to enhance specific properties of polymers such as mechanical, thermal, barrier, and fire retardant properties. The nanofillers show special properties for their size and high relative surface area to volume ratio. The optical clarity for spherical nanosize particle is better than equivalent conventional-size nanofiller because the diameter of spherical nanosize particle is smaller than the wavelengths of light. Since, nanofillers have larger specific surface area, then it creates more interaction with its surroundings and increased thermodynamic stability of the polymer as well as physical properties of the composite. Polymer composite can be defined as a polymer-nanofiller system in which the inorganic filler is on a nanometric scale at least in one dimension. In composite, the polymer and the nanofillers are associated through covalent bond which can be formed during *in-situ* polymerization (the monomer or the growing polymer chain can react with the filler particle), or processing of composite. Uniform dispersion of nanofiller in the polymer matrix is desired for better interaction between the polymer and the nanofiller to avoid phase separation and agglomeration of the nanofiller.

### Electron tunneling and hopping

In polymer composites, the electrical resistance involved a network of conducting and insulating phases where large number of resistors united in series and parallel. The electron hopping and tunneling mechanism affect on the magnitude of the overall conductance [219]. The polarization of charge is observed at the interface after applying electric field in between the electrodes due to the differences of electrical properties or resistivity among them [220]. As stated, electrons spontaneously moved from one localized state to another through electron tunneling and hopping conduction mechanism at a specific low temperature. For hopping process, a charge carrier moved suddenly from one occupied state to another equivalent empty donor state of higher energy [221]. Hopping conduction was generated due to defects or impurities which formed potential wells such as traps or localized states. This potential wells favor the electrons and ions charge carriers for hopping conduction. The degree of hopping conductivity depended on the concentration of donor and acceptor atom in the composites. The frequency of the field influenced the hopping rate if alternating voltage is applied, [222]. In general, the tunneling distance is in nanometer range, the average distance among the adjacent nanofillers [223]. The conductivity of composites depends on the tunneling mechanism. The electrical conductivity is generated due to electron transport among the neighboring nanofillers which indicate the leading conducting elements across the inter-particle tunneling distance [224].

### Percolation and conductivity

For the measurement of electrical conductivity of the conducting polymer composites, a term will definitely come, known as percolation. The percolation is related with conductivity and taken part a crucial role in conductor-insulator transition in the composite. The electrical conductivity of the polymer composite strongly varied with the concentration of the nanofillers [225], discussed earlier. At low nanofiller loading, composite behaves like an insulating material and increased gradually with increasing the nanofiller loading. At the percolation threshold, the concentration of the nanofiller is sufficient for the formation of continuous conducting network paths throughout the host polymer and observed high electrical conductivity of composites. The percolation threshold has been calculated theoretically with the help of the following power law equation [226]:

$$\sigma_{DC}(p) = \sigma_0(p - p_c)^t \quad \text{For } p > p_c$$

where,  $p_c$  represents the percolation threshold and  $t$  signifies the critical exponent.

### Percolation models theory

Last few decades, many researchers have approached several modeling for the percolation phenomenon [227,228]. Finally, they have decided two primary formulations for finding exact and approximate values of the percolation thresholds for different systems.

### Theory for lattice modeling

The lattice modeling is the one of the formula for finding the percolation threshold. The common lattice models for two dimensions are square, triangular, and honeycomb structures. For three dimensions, cube and diamond structures are common lattice models [229]. Lattice models explain percolation problems using the concepts of sites and bonds [230].

### Theory for bond percolation

The bond percolation is the simplest model where the lattice edges are chosen as the relevant entities.

### Theory for site percolation

In the case of site percolation, the lattice vertices are regarded as the relevant entities. Bond percolation can be converted to site percolation through placing a site on each bond and then fixed the sites with the closest neighbors [231].

### Theory for continuum modeling

Continuum models are more flexible for modeling the percolation of the polymer composites. In this modeling system, the geometrical objects can be placed randomly and individually in any spot of the continuum space and the overlap of the objects is defined as connectivity [232]. Three types of continuum modeling are observed:

### Theory for soft-core modeling

In the soft-core modeling, the fibers are modeled as fully interpenetrating objects. The major disadvantage of this approach is that solid nanofiller particles may touch each other but they cannot be merged.

### Theory for hard-core modeling

In the hard-core modeling, simulates particles has been argued to yield a better simulating result for conductivity behavior in real applications.

### Theory for hard-core with soft-shell modeling

In the case of hard-core with soft-shell modeling, the electrical percolation threshold depends on the geometry of the conducting particles as well as the tunneling distance between inclusions. In this modeling, the conductive fibers are considered to be composed of a hard core and a soft shell. The hard-core is tightly packed and signifies the actual conducting fiber. The penetrable soft shell which surrounds the hard core is aimed to represent the effective range of electron transferring in the matrix polymer. Here, the shell thickness is needed for modeling which is very much complicated and it is difficult to derive through analysis or experiments. Generally, this modeling is more computationally costly.

### Interaction forces between nanofillers

Generally, three types of interaction are possible between the nanofillers such as (i) van der Waals interactions, (ii) electrical double-layer interactions, and (iii) steric

interactions [233]. Besides this, hydrophobic and solvation forces play an important role between the nanofillers.

#### ***Van der Waals force interaction***

Among three interaction parameters, the van der Waals force is one of the most significant interactions between two identical spherical nanofillers which resists the dispersion of nanofillers. Theoretically, Hamaker equation has been expressed to calculate the van der Waals force interaction among spherical nanofillers [234].

$$F_{disp} = AR/12D^6$$

where,  $F_{disp}$  represents the van der Waals force, A stands for the Hamaker constant, R signifies the radius of the spherical nanofillers and D ( $D < 10-100$  nm) is the distance between the two spherical nanofillers. All parameters are positive including Hamaker constant A, so van der Waals interaction will be always attractive. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) confirm the dispersion interactions and supported this power law. However, some anomalies are observed at low D (1–2 nm). This is due to the quantum chemical nature of interacting particles [235].

#### ***Electrical double-layer interaction***

Another interaction between nanofillers is electrical double layer interactions. The ionic charge of the nanofillers attracted oppositely charged interface and help to form a diffuse layer near the surface. The  $\Psi$  is the decay of the electrostatic potential which is the function of the  $h$  and can be expressed by the following exponential equation:

$$\psi = \psi_o \exp(-h/k_d)$$

The decay length is known by the inverse of the Debye-Huckel parameter  $k_d$ , which is the thickness of the electrical double layer. The value of  $k_d$  is directly proportional to  $(\sum Z_i^2 C_i)^{-1/2}$  Where,  $Z_i$  represent the charges of counter ions and  $C_i$  stands for their concentrations. So,  $k_d$  increases with decreasing of  $Z_i$  and  $C_i$ . From the intercept at zero separation, the surface potential  $\psi_o$  value is obtained.  $h$  represents the distance between the flat surface [236].

#### ***Steric interaction***

Steric interaction is one of the forces which act between the nanofillers. During preparation of polymer composite, some portion of the polymer chains are tightly adsorbed on the surface and other parts of the polymer chains run away from the surface into the medium. Thus, a strong repulsion interaction observed between two polymers when they come at a collision distance between nanofillers. So, concentration of the polymer molecules increases and this increased concentration of the polymer

help to enhance the osmotic pressure in the gap. However, this type of mechanism does not show in the case of homopolymer. For homopolymer, polymer chains either adsorbed strongly on the surface or extended away from the surface. This kind of phenomena is observed in the case of copolymer where polymer chain consists of two parts. One portion is strongly adsorbed and other portion is extended away from the surface. In general, block or graft copolymers are used for better adsorption. de Gennes [237] has approached a theoretically relation for the steric interaction,  $F(D)$  when two layers of a grafted or a block copolymer overlap and written by the following equation.

$$F(D) = \frac{\beta kT}{s^3} \left[ (2\delta/D)^{9/4} - (D/2\delta)^{3/4} \right]$$

Here, D represents the separation between the surfaces,  $\delta$  signifies the thickness of the polymer layer,  $k$  is well known as Boltzmann constant, T stands for the absolute temperature,  $s$  is the symbol for the separation between the ends of the terminally attached polymer chains, and  $\beta$  is a fitting parameter. The first portion of the equation represents the osmotic pressure of the polymer and the second part of the equation stands for the stretching of the polymer when the polymer is adsorbed on the surface.

#### ***Hydrophobic and solvation forces interaction***

Besides the above three interaction, hydrophobic and solvation forces also act in the nanoparticles. The solvation forces rose from the solvent molecules which are closed to the surface. In the case of water medium, water molecules are interconnected through hydrogen-bonded network with the hydrophilic surface. In this case, solvation force is required to split the hydrogen bonds and drive the solvent molecules away from the surface. Hydrophobic forces are acted by non-polar molecules such as proteins and surfactants in an aqueous medium. In aqueous medium, structure of water molecules changed around the non-polar molecules which are the reasons behind the hydrophobic forces [238]. This interaction is short, attractive and applicable over some water molecules.

Generally, two methods are approached for the stabilization of nanoparticle dispersion by overcoming large van der Waals interaction [239]. The first one is electrostatic stabilization which depends on charge separation and formation of electrical double layers in an aqueous environment. The double layer is distinguished through a surface charge which is developed due to an unequal distribution of counter and co-ions. Repulsion interaction occurred if the distance between two nanoparticles is smaller than twice the double-layer thickness. This is because of lack of formation of fully double layers and incomplete screening of the particle surface charge. The magnitude of the repulsion is varied with the electrolyte concentration, surface potential (or zeta potential) and the valence. The double layers are enlarged at low concentration of electrolyte and the repulsive energy becomes more than the van der Waals

attraction at intermediate distances which developed an energy barrier. This energy barrier resists the mutual approach of the nanoparticles. On the basis of this picture, the theory of colloid stability (DLVO theory) has been developed by many researchers [240,241].

### **Polymer dependent electrical conductivity**

The electrical conductivity of the polymer composites strongly varied with nature of the polymer, processing condition, miscibility or immiscibility nature of the blend and preparation method. These things strongly effect on the dispersion of the nanofillers. If the nanofillers are agglomerated in the composites, then composite will behave like an insulating material. Otherwise, large amount of nanofiller will require achieving electrical conductivity.

### ***Nature of the polymer***

The nature of the polymer plays a great role on the electrical conductivity of polymer composites. Polymers may be crystalline or amorphous in nature. The polarity, surface tension, molecular weight, melt viscosity and crystallinity of the polymer greatly affect on the percolation threshold of the composites [242]. The electrical conductivity of the composites increased with increasing the surface tension of the polymer. The high surface tension of the polymer decreases the polymer–nanofiller interfacial tension. Percolation threshold of the polymer composites decreases with increasing polarity of the polymer. The polarity of the polymer helped to better interaction between the polymer and nanofillers and increased the electrical conductivity. Semi-crystalline polymer shows higher electrical conductivity and lower percolation threshold than amorphous polymer [242]. The melt viscosity of the polymer also directly effects on the electrical conductivity of the polymer composites and the value of the conductivity increases with decreasing the melt viscosity of the polymer. If molecular weight of the polymer is high, then electrical conductivity will be low. This high molecular weight polymer chains resist the formation of conductive network.

### ***Processing method and conditions for preparation of composites***

Processing methods and conditions greatly affect the electrical conductivity as well as percolation threshold of the polymer composites through dispersion of the nanofillers. The blending methods have been discussed such as solution polymerization, *in-situ* polymerization method and melt blending method. If polymer composites are prepared above the processing temperature of the polymer, then electrical conductivity of the polymer composites will be increased. At high temperature, melt viscosity of the polymer will be reduced and dispersion of the nanofiller will be better throughout the polymer. The dispersion of the nanofiller also depends on the speed of the extruder (rpm) and electrical conductivity varies with rpm.

### ***Effect of immiscible polymer blends***

The electrical conductivity of the polymer composites also depend on the polymer blend when two different polymers are used. As observed, the electrical conductivity of the polymer composites was achieved at low nanofiller loading in CB filled immiscible polymer blends [243,244]. In the case of immiscible polymer blend, nanofillers have different affinity to each polymer in the polymer blend and selectively distributed in the one of the polymer phases [243]. This kind of phenomena is well known as double percolation phenomena. Chen et al. [244] prepared immiscible polymer blend/nanofiller composites in the presence of graphite nanosheet with high electrical conductivity. The double percolation phenomenon was observed due to immiscible polymer blend which help to increase the electrical conductivity of the composites [245]. The obtained percolation threshold value of (50/50) HDPE/PMMA/VGCNF composites was lower than those of single polymer composites. The similar type of morphology was observed in the case of CB filled (70/30 w/w) PP/PS composites where CB nanofiller was located in the PS phase [246].

### **Preparation methods of polymer composites**

In general, three different methods have been greatly considered for the preparation of polymer composites. Depending of molecular weight of the polymers, polarity, reactivity of the polymers and nanofillers, these three methods are chosen for the preparation of composites. These methods are described with their advantages and disadvantages in details.

### ***In-situ polymerization***

*In-situ* polymerization method is the one of useful methods for the preparation of polymer composite. This method involved dispersion of the CNT/graphene in monomer using ultra-sonication, followed by addition of suitable initiator (Benzoyl peroxide or AIBN etc.). Then polymerization was done either by heat or radiation [247]. This method helps to make a strong interaction between the polymer matrix and nanofiller. Thus, a strong interconnected conducting network structure of nanofillers (CNT/graphene) has been developed throughout the matrix after polymerization. This method is very useful, eco-friendly and industrially feasible for the preparation of conducting polymer composites. This method is used for the polymers which cannot be processed by solution or melt mixing, e.g., insoluble and thermally unstable polymers. A variety of polymer composites have been prepared using this method, i.e. PS/graphene [248], PMMA/EG [249], PI/graphene [250], etc.

Hu et al. [248] synthesized graphene-reinforced PS composites by *in-situ* polymerization. Wang et al. [249] prepared PMMA/EG composites through *in-situ* polymerization technique. Hornbostel et al. [251] reported the percolation threshold of PC/MWCNT composites in between 1.5 and 2.0 wt% of MWCNT loading. Pan et al. [252] prepared nylon 6/EG composites by *in-situ*

polymerization method. Saeed et al. [253] prepared PCL/MWCNT composites through *in-situ* polymerization method. Harrison et al. [254] synthesized PI/SWCNT composites by *in-situ* polymerization.

### **Solution blending**

Solution blending is one of the techniques for the preparation of the polymer composite where solvent taken part a major role. This method provided that polymer first dissolved in the suitable solvent followed by CNT/graphene is allowed to swell in the same solvent [2]. CNT/graphene are dispersed by ultra-sonication in a suitable solvent, such as water, acetone, chloroform, DCM, THF, DMF or toluene and then, dissolved polymer is added to this suspension of the nanofillers. The polymer then adsorbed onto the delaminated nanofillers and polymer composites have been prepared by the evaporation of the solvent. The driving force for polymer intercalation from solution is the entropy gained by desorption of solvent molecules, which compensates for the decrease in conformational entropy of the intercalated polymer chains. Therefore, a relatively large number of solvent molecules need to be desorbed from the nanofiller to accommodate the incoming polymer chains. This method is useful for the synthesis of intercalated polymer composites based on polymers with low or even no polarity. Epoxy-based composites can be synthesized using this technique but removal of the solvent is major problem. The proper dispersion and distribution of the pristine CNT or graphene is very difficult in a solvent by simple magnetic stirring. A high power ultra-sonication process is more effective for the better dispersion of CNT or graphene in the solvent. Ultra-sonication has been extensively used for the dispersion, crushing, emulsifying, and activating the nanofillers. However, major drawback of multi-effects of ultrasound ultra-sonication is that the aggregates and entanglements of CNT or graphene can be effectively broken down in this high ultrasonic irradiation.

For example, Deleuze et al. [255] prepared epoxy/EG composites using solution blending method. Zheng et al. [256] prepared PMMA/EG composites by solution blending. Stankovich et al. [257] prepared PS/graphene composites through solution casting method. Khatua et al. [258] prepared PMMA/MWCNT composites through *in-situ* polymerization of methyl methacrylate in the presence of commercial PMMA bead. Khatua et al. [259] also prepared PS/MWCNT composites in the presence of PS-GNP bead through *in-situ* polymerization of styrene monomer. Spitalsky et al. [260] prepared epoxy/oxidized MWCNT composites by solution blending procedure.

### **Melt blending**

Melt blending is one of simple and cost effective method for the preparation of polymer composite. This method provided melt mixing of polymer in the presence of nanofillers (CNT or graphene) at the processing temperature of the polymer. The advantage of this method is that solvent is not required for the preparation of the composite. Generally, extrusion and injection molding are

used for mechanically mixing of polymer with CNT/graphene at the processing temperature of the polymer. This method is very much applicable for the preparation of thermoplastic polymer composites for its low cost and it is very industrially feasible method. Melt intercalation method is very much useful for those polymers which are unsuitable for adsorption or *in-situ* polymerization.

A wide range of polymer composites, such as PET/graphene [261], HDPE/EG [262], SAN/MWCNT [263,264] etc have been prepared using this method. Zhang et al. [261] prepared PET/graphene composites using melt mixing of PET and graphene at the processing temperature of PET. Wong et al. [262] prepared HDPE/EG composites through melt blending method. Goldel et al. [263] prepared SAN/MWCNT composites by melt mixing with high electrical conductivity. Sathpathy et al. [265] have studied the electrical conductivity of melt blended PC/MWCNT composites and an electrical conductivity of  $\sim 2 \times 10^{-8} \text{ S}\cdot\text{cm}^{-1}$  was achieved at 2 wt% loading of MWCNT, prepared by diluting a PC/MWCNT (15 wt%) mixture. Yoon et al. [266] have studied the electrical percolation of melt blended PC/MWCNT composites prepared by diluting a PC/MWCNT mixture containing 20 wt% loading of MWCNT. They have shown the percolation threshold at  $\sim 3$  wt% MWCNT loading in the PC/MWCNT composites. Micusik et al. [267] prepared PP/MWCNT composites through melt blending method.

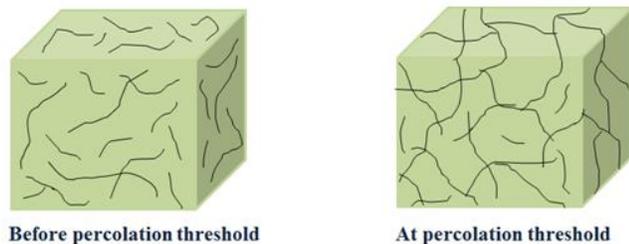
### **Polymer/CNT composites**

A number of polymer/CNT composites have been reported based on various CNTs such as SWCNT, MWCNT or functionalized CNT, using different polymers as the matrix. Depending on the nature of the polymer, CNT or processing conditions, obtained electrical conductivity values of the composites are different. The different types of polymer/CNT composites have been prepared based on various polymers such as epoxy [268], PS [269], PMMA [270], PCL [253], PE [271], PC [272] etc. Thus, polymer/CNT composites have been prepared using solution, *in-situ* or melt blending method.

### **PC/CNT composites**

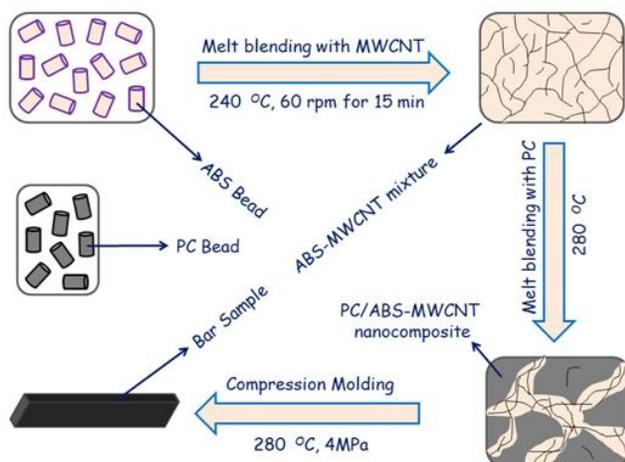
Hornbostel et al. [251] have observed the electrical conductivity of the PC/MWCNT composites, prepared by melt blending. They reported that the composite shows the percolation threshold in between 1.5 and 2.0 wt% of MWCNT loading. Sathpathy et al. [265] have worked on PC/MWCNT composite for the measurement of electrical conductivity of the composite. They have prepared composite through melt blending technique. They have achieved electrical conductivity of  $\sim 2 \times 10^{-8} \text{ S}\cdot\text{cm}^{-1}$  at 2 wt% MWCNT loading. Yoon et al. [266] have reported the electrical conductivity of the PC/MWCNT composite. They have measured the electrical conductivity and percolation threshold of the composite. The reported percolation threshold is  $\sim 3$  wt% loading of MWCNT.

**Fig. 12** shows the schematic representation for the orientation of the conducting nanofillers (MWCNT) before and at the percolation threshold in the composites. At the percolation threshold, a conducting network path of MWCNT is developed which is the reason behind the sudden increase in electrical conductivity of the composites.



**Fig. 12.** A schematic presentation for the arrangement of nanofillers before percolation threshold and at percolation threshold in polymer composites.

Khatua et al. have studied the electrical conductivity of different PC/MWCNT composites [272-277] to achieve high electrical conductivity at low MWCNT loading with very low percolation threshold. They have prepared PC/MWCNT composites by melt dilution of PC with ABS/MWCNT mixture [272]. The very high electrical conductivity of  $\sim 1.49 \times 10^{-6} \text{ S.cm}^{-1}$  was achieved at very low MWCNT loading of  $\sim 0.328 \text{ vol}\%$ . The percolation threshold of the composites was observed at very low loading ( $0.195 \text{ vol}\%$ ) of MWCNT due to double percolation phenomenon for immiscible nature of PC and ABS in the blend. This plays a major role to get high electrical conductivity at such low MWCNT loading. In PC/ABS-MWCNT composite, MWCNTs were selectively localized in the ABS phase. **Fig. 13** represents schematical diagram for the preparation of PC/ABS-MWCNT composite. The electrical conductivity improved with increasing the MWCNT loading. The thermal properties of composite are greatly affected in the presence of MWCNT.



**Fig. 13.** Schematic representation for the preparation of PC/ABS-MWCNT composites. [Reproduced with permission from Polymer Composites, vol. 34(4), p. 570, Copyright (2013) Society of Plastics Engineers, (Reference 272)].

Khatua et al. have also prepared PC/PMMA-MWCNT composites by melt dilution of PMMA-MWCNT master batch with pure PC in different ratios to investigate the electrical conductivity of the composites [273]. The reported electrical conductivity of  $\sim 3.74 \times 10^{-5} \text{ S.m}^{-1}$  was achieved at very low ( $\sim 0.37 \text{ wt}\%$ ) loading of MWCNT. The PC and PMMA form a miscible blend in the composite. They also studied the electrical conductivity of the PC/PBT-MWCNT composites through same melt blending method [274]. In this study, they have found that PC/PBT blend is immiscible in nature and becomes miscible in the presence of MWCNT. MWCNT acts as a viscosity modifier and the melt viscosity of PBT-MWCNT mixture become almost equal with melt viscosity of PC in presence of MWCNT. Thus, no phase separation was observed in PC/PBT-MWCNT composite. The observed conductivity was  $\sim 6.87 \times 10^{-5} \text{ S.m}^{-1}$  at very low ( $\sim 0.35 \text{ wt}\%$ ) loading of MWCNT. The glass transition temperature ( $T_g$ ) and storage modulus of the blend also increased in the presence of small amount of MWCNT. Khatua et al. [275] also studied the electrical conductivity of PC/MWCNT composites in the presence of SAN copolymer. PC/SAN blend is immiscible with or without MWCNT. In their study, high electrical conductivity was obtained at low MWCNT loading due to selective dispersion of MWCNT in SAN phase. The double percolation phenomena were observed for this composite. The electrical conductivity of  $\sim 1.38 \times 10^{-3} \text{ S.m}^{-1}$  was reported at  $\sim 0.35 \text{ wt}\%$  loading of MWCNT. They also observed the electrical conductivity of the PC/MWCNT composites in the presence of PCL [276] using similar melt dilution method. In this case, they have got conductivity of  $\sim 1.83 \times 10^{-1} \text{ S.m}^{-1}$  at low ( $\sim 0.7 \text{ wt}\%$ ) loading of MWCNT. The low melt viscosity of PCL taken part a crucial role for homogeneous dispersion of MWCNT throughout the polymer phase. They also studied the electrical conductivity of PC/MWCNT composites by increasing the processing temperature of the polymer [277]. In this study, they have prepared PC/MWCNT composites at two different temperatures ( $280$  and  $350 \text{ }^\circ\text{C}$ ). At  $350 \text{ }^\circ\text{C}$  (above the processing temperature of PC), high electrical conductivity was observed compared to electrical conductivity of PC/MWCNT composite which was prepared at the processing temperature of PC ( $280 \text{ }^\circ\text{C}$ ). The reported electrical conductivity was  $\sim 1.38 \times 10^{-1} \text{ S.m}^{-1}$  at  $350 \text{ }^\circ\text{C}$  in presence of  $0.5 \text{ wt}\%$  of loading MWCNT loading with very low percolation threshold ( $0.11 \text{ wt}\%$ ). The thermal properties of PC were much increased with the incorporation of MWCNT.

### PS/CNT composites

Khatua et al. [259] have reported PS based composite which has been prepared in the presence of GNP and MWCNT. In their study, they used different method for the preparation of PS/GNP/MWCNT composite. Initially, they have synthesized PS-GNP micro bead through suspension polymerization of styrene in the presence of

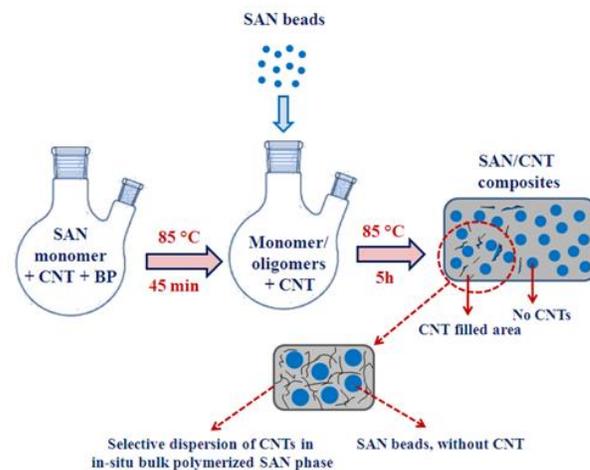
GNP. Then, PS/GNP/MWCNT composites were prepared through bulk polymerization of styrene with MWCNT in the presence of PS-GNP micro beads. Thus, the composites with different MWCNT and GNP loading have been prepared by varying the MWCNT loading as well as PS-GNP micro bead loading in the composites. The composite with 0.3 wt% loading of MWCNT and 0.29 wt% GNP loading shows electrical conductivity of  $\sim 9.75 \times 10^{-3} \text{ S.cm}^{-1}$ . This high value of conductivity suggested the formation of possible GNP-CNT-GNP or CNT-GNP-CNT conducting path throughout the host polymer. Khatua et al. also studied PS/MWCNT composites in the presence of commercial PS beads and composite has been prepared by *in-situ* bulk polymerization [269]. They explained that commercial PS bead acts as excluded volume in the composite where MWCNT cannot penetrate during polymerization. Thus, MWCNT was dispersed selectively in the *in-situ* polymerized PS region and helped to achieve high electrical conductivity. They also reported that conductivity value strongly depended on the MWCNT loading as well as commercial PS bead loading. Thus, the reported electrical conductivity of the composite with 0.26 wt% loading of MWCNT in the presence of 70 wt% PS bead was  $\sim 1.48 \times 10^{-1} \text{ S.m}^{-1}$ .

#### PMMA/CNT composites

Khatua et al. [258] discussed about the PMMA based composite. The composite has been synthesized through bulk polymerization of MMA in presence of MWCNT and commercial PMMA bead. In their method for the preparation of composite, the obtained conductivity value was  $\sim 4.71 \times 10^{-3} \text{ S.m}^{-1}$  which was achieved at 0.2 wt% loading of MWCNT. The used commercial PMMA bead behaved as an excluded volume which plays an important role to enhance the MWCNT concentration in the *in-situ* polymerized PMMA region as well as electrical conductivity of the composite.

#### Epoxy/CNT composites

Spitalsky et al. [260] have reported epoxy based composite which has been prepared in presence of oxidized MWCNT through solution blending. They have studied the electrical, thermal and rheological properties of the composites and observed that all properties improved significantly with increasing the CNT loading. In the composite, dispersed CNT hold more interfaces with polymer for its high surface area and make a strong covalent bonding with polymer. Thus, chain mobility of the epoxy polymer was affected and increased the thermal as well as mechanical properties of the polymer in presence of CNT. Youn et al. [272] also studied the electrical, mechanical, rheological and thermal properties of epoxy/MWCNT composites. They followed solution blending method for the preparation of composite.



**Fig. 14.** Schematic representation for the *in-situ* preparation of SAN/MWCNT composites in the presence of SAN beads. [Reproduced with permission from Ind & Eng Chem Res, vol. 52(8), p. 2558, Copyright (2013) American Chemical Society, (Reference 300)].

#### SAN/CNT composites

Several works have already done on SAN/CNT composite. Lee et al. [117] have used SAN polymer for the preparation of SAN/MWCNT composite. In their study, they used simple and cost effective melt blending method for the preparation of composite. They have studied the electrical conductivity of the composite and reported value was  $\sim 4 \times 10^{-4} \text{ S.cm}^{-1}$  at 2 wt% MWCNT loading. Gultneret et al. [129] have chosen amino-functionalized MWCNT for the preparation of SAN/CNT composite. They also preferred melt mixing method over other methods. They suggested that properties of CNT increased for functionalization. They obtained electrical conductivity of  $\sim 5 \times 10^{-4} \text{ S.cm}^{-1}$  at 1.0 wt% loading of functionalized CNT. Also, thermal properties significantly increased in the presence of modified MWCNT. Khatua et al. [300] also studied SAN based composite in different technique. In their method, composite has been synthesized by *in-situ* bulk copolymerization of styrene and acrylonitrile in the presence of MWCNT. At the end of bulk copolymerization, they added commercial SAN bead to this highly viscous solution and dried. By this different composite preparation technique, they achieved conductivity of  $\sim 8.07 \times 10^{-5} \text{ S.cm}^{-1}$  at 0.1 wt% loading of CNT in presence of 70 wt% SAN bead. The conductivity of the composites strongly depended on the SAN bead loading as well as CNT concentration. The size of the SAN beads also affected on the conductivity value, they discussed in their study. They have proposed a schematic diagram for the preparation of the composites, as shown in Fig. 14.

**Table 2** summarizes the electrical conductivity of different polymer/CNT composites depending on the processing method, matrix polymer and nature of the nanofiller.

**Table 2.** Electrical Conductivity of different polymer/CNT composites.

Matrix	CNT Type	Processing Method	CNT loading (wt%)	Electrical Conductivity (S.m <sup>-1</sup> )	Reference Number
PC/ABS	MWCNT	Melt mixing	1.188 vol%	$\sim 7.23 \times 10^{-1}$	[272]
PC	MWCNT	Melt mixing	5	$\sim 1.0$	[29]
PC/PMMA	MWCNT	Melt mixing	0.37	$\sim 3.74 \times 10^{-5}$	[273]
PC/PBT	MWCNT	Melt mixing	0.35	$\sim 6.87 \times 10^{-5}$	[274]
PC/SAN	MWCNT	Melt mixing	0.35	$\sim 1.38 \times 10^{-3}$	[275]
PC/PCL	MWCNT	Melt mixing	0.70	$\sim 1.83 \times 10^{-1}$	[276]
PC	MWCNT	Melt mixing	0.50	$\sim 1.38 \times 10^{-1}$	[277]
PC	Pristine MWVNT with P3HT-g-PCL Compatibilizer	Solution blending	5	$\sim 6.4 \times 10^1$	[278]
PC	MWCNT	Melt mixing	5	$\sim 1 \times 10^1$	[279]
	SWCNT		1	$\sim 1 \times 10^{-2}$	
PC	PPE-functionalized SWCNT	Solution mixing	7	$\sim 4.8 \times 10^2$	[280]
PC	MWCNT	Melt mixing	15	$\sim 20$	[281]
PC	MWCNT	Melt mixing	3	$\sim 5$	[282]
PC	MWCNT	Melt mixing	15	$\sim 1 \times 10^1$	[283]
PC	MWCNT	Melt blending	15	$\sim 10^3$	[284]
PC	MWCNT	Melt mixing	15	$\sim 10$	[285]
PC	MWCNT	Melt mixing	15	$\sim 10^2$	[286]
PP/HDPE	MWCNT	Melt mixing	0.60	$\sim 10^{-4}$	[287]
PMMA	MWCNT	Spin coating	16	$\sim 10^{-3}$	[288]
PMMA	MWCNT	<i>In-situ</i>	0.2	$\sim 4.71 \times 10^{-3}$	[258]
PMMA	MWCNT	Solution mixing	0.3	$\sim 10^3$	[289]
PMMA	MWCNT	Electrospinning	2	$\sim 5.3 \times 10^{-2}$	[290]
PMMA	SWCNT	Solution mixing	8	$\sim 70$	[291]
PMMA	SWCNT	Solution mixing	1.4	$\sim 50$	[270]
PMMA	SWCNT	Coagulation method	2	$\sim 5 \times 10^{-3}$	[292]
PMMA	SWCNT	Coagulation method	7	$\sim 1 \times 10^{-2}$	[293]
PMMA	Aligned CNT	Drop casting		$\sim 12.5 \times 10^1$	[294]
PMMA	MWCNT	Solution mixing	0.4	$\sim 3 \times 10^3$	[295]
PS	SWCNT	Solution mixing	2	$\sim 1 \times 10^{-3}$	[296]
PS	MWCNT/GNP	<i>In-situ</i>	0.3	$\sim 9.75 \times 10^{-1}$	[259]
PS	MWCNT	<i>In-situ</i>	0.26	$\sim 1.48 \times 10^{-1}$	[269]
PS	Pristine SWCNT	Solution mixing	2	$\sim 1 \times 10^{-1}$	[297]
PS	PPE-functionalized SWCNT	Solution mixing		$\sim 6.89$	[280]
PS	Aligned CNT	Drop casting		$\sim 13.3 \times 10^2$	[294]
PS	PmPV coated SWCNT	Solution mixing	1.5	$\sim 2 \times 10^{-7}$	[298]
PS	MWCNT	Solution mixing	1.5	$\sim 1$	[299]
SAN	MWCNT	<i>In-situ</i>	0.10	$\sim 1.38 \times 10^{-4}$	[300]
Epoxy	MWCNT	Solution mixing	1.4	$\sim 0.5$	[268]

Epoxy	MWCNT	Calendaring process	0.5	~0.01	[301]
Epoxy	MWCNT	Calendaring process	5	~50	[302]
Epoxy	MWCNT	Solution mixing	10	$\sim 3 \times 10^{-3}$	[303]
Epoxy	MWCNT	Roll milling	0.75	$\sim 1 \times 10^{-1}$	[304]
Epoxy	MWCNT	Solution mixing	0.18	$\sim 4 \times 10^{-1}$	[305]
Epoxy	MWCNT	Bulk mixing	4	$\sim 2 \times 10^{-1}$	[306]
Epoxy	Oxidized MWCNT	Solution mixing	1	$\sim 1 \times 10^{-2}$	[260]
Epoxy	Pristine MWCNT	Solution mixing	1	$\sim 1 \times 10^{-2}$	[307]
Epoxy	SDS suspended MWCNT	Bulk mixing	0.5	$\sim 2.5 \times 10^{-7}$	[308]
Epoxy	Aligned MWCNT	Shear mixing	0.01	~2	[213]
Epoxy	MWCNT	Solution mixing	12	$\sim 5 \times 10^{-5}$	[309]
Epoxy	MWCNT	High shear mixing		~0.8	[310]
	Alkali treated SWCNT			~0.05	
Epoxy	SWCNT/DWCNT	Solution mixing	0.4	$\sim 1 \times 10^{-2}$	[311]
Epoxy	SWCNT	Ultra-sonication		$\sim 1.25 \times 10^{-3}$	[312]
Epoxy	SWCNT	Solution mixing	15	~10	[23]
Epoxy	CNT	Solution mixing	2.5	$\sim 1.3 \times 10^{-2}$	[313]
Epoxy	Acid modified CNT	Mechanical mixing		$\sim 6.9 \times 10^{-3}$	[314]
PE	MWCNT	Melt blending	10	$\sim 1 \times 10^{-3}$	[271]
LDPE	MWCNT	Ball milling	10	~2	[315]
HDPE	SWCNT	Fast crystallization	8	$\sim 7 \times 10^1$	[316]
HDPE	SWCNT	Melt extrusion	5	$\sim 1 \times 10^{-1}$	[317]
UHMWPE	MWCNT	Solution mixing		~10.7	[318]
UHMWPE	MWCNT	Solution mixing	15	~6	[319]
UHMWPE	MWCNT	Solution mixing		$\sim 5 \times 10^{-1}$	[320]
UHMWPE	MWCNT	Solution mixing		~0.6	[321]
UHMWPE	SWCNT	Dry mixing	2	$\sim 1 \times 10^{-2}$	[322]
UHMWPE/LM WPE 1:1	MWCNT	Solution mixing		~1.5	[318]
UHMWPE/LM WPE 1:2				~0.7	
UHMWPE/LM WPE 6:1	MWCNT	Solution mixing		$\sim 1 \times 10^{-1}$	[321]
PP	MWCNT	Melt mixing	10.7	~4.6	[267]
PP	MWCNT	Melt blending	5	~0.5	[323]
PP	SWCNT	Powder compression		~8	[324]
PVA	MWCNT	Solution mixing	22.5	~0.27	[325]
PVA	CNT	Solution mixing	60	$\sim 1 \times 10^2$	[326]
PVC	MWCNT	Mechanical mixing		$\sim 1 \times 10^{-2}$	[327]
PVAc	MWCNT	Solvent casting	5	$\sim 2.9 \times 10^{-6}$	[328]
PVAc	Modified SWCNT	Emulsion mixing		~20	[329]
PCL	MWCNT	<i>In-situ</i> polymerization	7	~10	[253]
PCL	SWCNT	Solution mixing	3	$\sim 2 \times 10^{-3}$	[330]

PLLA	MWCNT	Solution mixing		~0.4	[331]
PLLA/PCL 3:7	Oxidized MWCNT	Melt mixing	3	$\sim 1 \times 10^{-5}$	[332]
P3HT	MWCNT	Solution mixing	36	~70	[333]
P3HT	MWCNT	Solution mixing	30	$\sim 5 \times 10^{-1}$	[334]
P3HT	Undoped MWCNT	<i>In-situ</i> oxidative polymerization		$\sim 3.56 \times 10^{-1}$	[335]
P3HT	I <sub>2</sub> doped CNT	Solution mixing		$\sim 1 \times 10^{-4}$	[336]
P3OT	MWCNT	Solution mixing	0.05	$\sim 5 \times 10^{-2}$	[337]
P3OT	SWCNT	Solution mixing		$\sim 1 \times 10^{-3}$	[338]
P3OT	SWCNT	Solution mixing	35	~0.05	[339]
Nylon 6	MWCNT	Melt mixing	5	~0.01	[340]
Nylon 6	Modified MWCNT	Melt mixing	2	$\sim 1 \times 10^{-3}$	[341]
Nylon 66	MWCNT	Melt mixing	5	~0.1	[340]
NyloN 610	Modified MWCNT	<i>In-situ</i> interfacial polymerization		$\sim 6.1 \times 10^{-10}$	[342]
PI	MWCNT	<i>In-situ</i> polymerization	6.68 vol%	~10	[343]
PI	MWCNT	Solution mixing	3	~10	[344]
PI	SWCNT	<i>In-situ</i> polymerization	1.3	$\sim 1 \times 10^{-4}$	[254]
PI	SWCNT	<i>In-situ</i> polymerization	5	$\sim 1 \times 10^{-3}$	[345]
PI	Unmodified MWCNT	Solution mixing	6.98	$\sim 2.4 \times 10^{-3}$	[346]
	Acid modified MWCNT			$\sim 3.8 \times 10^{-6}$	
	Amine modified MWCNT			$\sim 5.8 \times 10^{-6}$	
LMW-PI	SWCNT	Solution mixing	1	$\sim 2.9 \times 10^{-8}$	[347]
HMW-PI				$\sim 1.6 \times 10^{-6}$	
PU	MWCNT	Solution mixing	27	$\sim 2 \times 10^3$	[348]
PU	MWCNT	<i>In-situ</i> polymerization		~30	[349]
PU	Modified MWCNT	melt mixing	5	$\sim 1 \times 10^{-1}$	[97]
WBPU	Acid treated MWCNT	Solution blending		$\sim 8 \times 10^{-2}$	[350]
PET	SWCNT	Melt mixing	5	$\sim 1 \times 10^{-4}$	[351]
PET	SWCNT	Melt mixing	3	$\sim 1 \times 10^0$	[352]
		<i>In-situ</i> polymerization	0.3	$\sim 1 \times 10^{-2}$	
PETI	MWCNT	Ball milling	15	$\sim 4 \times 10^{-3}$	[353]
SE	Functionalized MWCNT	Mechanical mixing		$\sim 1 \times 10^1$	[354]
SE	CNT mat	Spin coating		$\sim 4 \times 10^{-4}$	[355]
SE	CNT mixture	Grinding mixing	3.8	~3.6	[356]
PDMS	MWCNT	Ultrasonic agitation	2.5	~0.02	[357]
PDMS	SWCNT	Solution mixing		$\sim 1 \times 10^2$	[358]
PHET	Oxidized MWCNT	Solution mixing		$\sim 1.38 \times 10^{-2}$	[359]
PTH	SWCNT	<i>In-situ</i> chemical oxidative		~41	[360]

		polymerization			
PEMA	SWCNT	<i>In-situ</i>	23	~0.4	[361]
		polymerization			
EMMA	MWCNT	Solution mixing		~10	[321]
SIBS	SWCNT	Solution mixing	0.3	$\sim 8.5 \times 10^2$	[362]
SBA	MWCNT	Suspension mixing	5.4	~20	[363]
SBA	MWCNT	Solution mixing	15	~1	[364]
SBR	MWCNT	Solution mixing	12	~200	[365]
Natural rubber	SWCNT	Roll milling	10	~1	[366]
Styrene– isoprene copolymer latex	SWCNT	Mini emulsion		$\sim 9 \times 10^{-5}$	[367]
Poly [styrene-b- (ethyleneco- butylene) -b-styrene]	MWCNT	Melt blending		$\sim 5.16 \times 10^2$	[368]
Nafion	SWCNT	Solution mixing	18	$\sim 3.2 \times 10^3$	[369]
PmPV	MWCNT	Solution mixing	0.35	$\sim 1 \times 10^{-2}$	[370]
PmPV	CNT	Solution mixing	<10	~3	[371]
PmPV	CNT	Solution mixing	36	~3	[372]
PVDF	Modified MWCNT	Solution mixing		$\sim 1 \times 10^{-2}$	[373]
PPS	MWCNT	Powder mixing & compression	5.4	$\sim 1 \times 10^3$	[374]
PPY	MWCNT	<i>In-situ</i> $\gamma$ radiation induced polymerization		~38	[375]
PPY	MWCNT	<i>In-situ</i> chemical oxidative polymerization		$\sim 3.89 \times 10^2$	[376]
PPY	MWCNT	<i>In-situ</i> inverse microemulsion polymerization	30	~40	[377]
PPY	CNT	<i>In-situ</i> polymerization		$\sim 1.6 \times 10^3$	[378]
PPY	CNT	<i>In-situ</i> chemical oxidative polymerization		$\sim 2.31 \times 10^3$	[379]
PANI	MWCNT	<i>In-situ</i> polymerization		~10	[380]
PANI	MWCNT	<i>In-situ</i> emulsion polymerization	10	~6.6	[381]
PANI	MWCNT	<i>In-situ</i> oxidative polymerization	24.8	$\sim 1.27 \times 10^2$	[382]
PANI	SWCNT	electrochemical polymerization	8	$\sim 1.56 \times 10^{-2}$	[383]
PANI	SWCNT	Solution mixing	15	$\sim 2 \times 10^3$	[384]
PEO	SWCNT	Solution mixing	0.5	$\sim 1 \times 10^{-2}$	[385]
PEI	SWCNT	Solution mixing		$\sim 2 \times 10^4$	[386]
PAN	Oxidized MWCNT	Solution mixing		~2.88	[387]
PA	MWCNT	Solvent mixing		~0.01	[388]
PA	SWCNT	Powder compression & hot molding	13	~10 <sup>2</sup>	[324]
PPS	MWCNT	Powder mixing & compression	5.4	~10 <sup>2</sup>	[374]

### Polymer/graphene composites

Graphene is most promising nanofillers in modern time, discussed earlier. Thus, graphene based polymer composite taken part a key role in modern science. The regular dispersion of nano-sized graphene throughout host polymer has played a big role for getting high impact polymer composite. In the presence of graphene and its derivatives in the polymer composite, the physical properties of the polymer changed significantly which opened the application area of polymers in various fields. For the preparation of polymer/graphene composite, several kinds of graphene and its derivatives have been used such as expanded graphite, graphene oxide and graphene etc [389-391] which have been discussed before. The graphene, expanded and exfoliated graphite have been used for the preparation of different polymer composites such as epoxy [392,393], PMMA [394], PS [395, 396], PC [397], PVA [398], PET [399], nylon 6 [400], PPS [401], and PANI [402] etc.

#### Epoxy/graphene composites

Djokovic et al. [389] have prepared epoxy based composite using expanded graphite (EG) nanosheet as nanofiller. They have selected solution blending method for the preparation of epoxy/EG composite. They have measured electrical conductivity and observed percolation threshold at 3 wt% loading of EG. Deleuze et al. [255] have studied the thermal conductivity of the epoxy/EG composite. They have also chosen solution blending method over other methods. They observed that thermal conductivity of the epoxy greatly affected in the presence of EG and increased with increasing the EG loading. The EMI shielding effectiveness of the composites increases with increasing the concentration of the graphene which formed a continuous conductive interconnected graphene-based sheet network structure in the insulating epoxy matrix. Thus, insulating epoxy matrix becomes electrically conductive in nature. Chen et al. [393] have studied epoxy based composite in the presence of functionalized graphene. They have preferred *in-situ* polymerization method for the preparation of the composite. They have studied EMI shielding effectiveness of the composite and reported value was ~21 dB at 8.8 vol% (15 wt%) loading of graphene. They also measured the electrical conductivity of the composite and percolation threshold was obtained at 0.52 vol% loading of graphene.

#### PS/graphene composites

Khatua et al. [259] have prepared PS composite using two nanofillers (GNP and MWCNT) in their system. The composite has been synthesized through *in-situ* bulk polymerization of styrene and MWCNT in presence of PS-GNP micro beads which have been synthesized by suspension polymerization of styrene in presence of GNP. They have studied EMI shielding as well as electrical conductivity of the composite at different CNT and GNP loading. Hu et al. [248] have used graphene nanosheet (GNS) for the preparation of PS/GNS composite. They

have considered *in-situ* emulsion polymerization for the preparation of composite. They have checked the thermal stability and electrical properties of the PS/GNS composite in their study with variation of GNS nanofiller. They observed electrical conductivity of  $\sim 2.9 \times 10^{-2} \text{ S.m}^{-1}$  when it was prepared with 2.0 wt% of GNS loading. Figure 15 shows a schematic diagram of the formation of the PS/GNS composites. Stankovich et al. [257] have reported the electrical conductivity of PS/graphene composite, prepared by solution blending. The reported conductivity value was  $\sim 1 \text{ S.m}^{-1}$  for composite at 2.5 vol% loading of graphene and percolation threshold was observed at 0.1 vol% loading of graphene. Yu et al. [395] have used octadecylamine (ODA) functionalized GO for the preparation of PS/GO composite. They have prepared composite via solution blending followed by compression molding. They studied the electrical conductivity and obtained value was  $\sim 4.6 \times 10^{-1} \text{ S.m}^{-1}$  at 0.92 vol% of GO loading. They explained that hydrophilic GO converted to hydrophobic ODA-functionalized GO in the presence of the long octadecyl chain, resulted better dispersion of GO in the composite.

#### PC/graphene composites

Macosko et al. [397] have studied electrical, thermal and mechanical properties of PC/graphite and PC/FGS composites. They used melt blending method (at 250 °C under N<sub>2</sub> purge) for the preparation of composite. They observed that electrical, thermal and mechanical properties of the composites were significantly enhanced in the presence of nanofillers.

#### PMMA/graphene composites

You et al. [249] have observed the electrical conductivity of PMMA/EG composite. The obtained value was  $\sim 60 \text{ S.cm}^{-1}$  at 8 wt% loading of EG. The composite has been prepared via *in-situ* polymerization of MMA in the presence of EG. Zheng et al. [256] have prepared PMMA based composite in the presence of EG through solution blending. Zhang et al. [394] have used graphene-13.2 (with C/O ratio of 13.2) for the preparation of PMMA/graphene composite. They have observed EMI shielding effectiveness as well as electrical conductivity of the composite. A high EMI shielding effectiveness of  $\sim 30 \text{ dB}$  was obtained at 4.2 vol% loading of graphene. The reported conductivity value was  $\sim 2.38 \times 10^{-2} \text{ S.m}^{-1}$  at very low loading of graphene (0.8 vol%).

#### PVA/graphene composites

Deng et al. [398] have prepared PVA/rGO composite by solution casting method. They have observed that electrical, mechanical and thermal properties of the pure PVA were greatly increased in the presence of rGO. They have shown that the electrical conductivity was greatly affected with the addition of rGO in the composite and measured value was  $\sim 2.5 \times 10^{-5} \text{ S.m}^{-1}$  at 0.7 wt% loading of rGo. In presence of rGO, chain mobility of the pure PVA was restricted through H-bonding with the -OH

groups of PVA moiety which helped to improve the mechanical and thermal stability of the composite.

#### **PET/graphene composites**

Li et al. [399] have observed the electrical and thermal stability of the PET/graphene composite. They used *in-situ* polymerization method for the preparation of the composite. They observed that thermal stability and conductivity value of the composite increased significantly with increasing the graphene loading during preparation of the composite. The homogeneous dispersion of graphene sheets throughout the polymer effectively reduced the percolation threshold and increased the conductivity value. Zhang et al. [261] used melt blending method for the preparation of PET/graphene composite. They have studied electrical conductivity of PET/graphene composite at various graphene loading. They observed electrical conductivity of  $\sim 2.0 \times 10^{-13} \text{ S.m}^{-1}$  at 0.47 vol% loading of graphene and  $\sim 7.4 \times 10^{-2} \text{ S.m}^{-1}$  at 1.2 vol% graphene loading. At high graphene loading, a strong interconnected conductive network path of graphene was developed throughout the matrix polymer which has played a crucial role to increase the electrical conductivity of the polymer composite.

#### **PANI/graphene composites**

PANI itself is an electrically conducting polymer. So, composite with graphene behaved like high electrically conducting material. Meng et al. [402] have prepared PANI/graphite composite through *in-situ* polymerization of aniline in the presence of graphite nanosheets. They have measured electrical conductivity of composite at various graphite loading. They have achieved electrical conductivity of  $\sim 33.3 \text{ S.cm}^{-1}$  at 1.5 wt% loading of graphite which was six times higher than that of pure PANI. In the composite, a strong  $\pi$ - $\pi$  interaction between the electron rich PANI and the aromatic structure of the graphite is developed which also helped to achieve high electrical conductivity at low nanofiller loading. The

thermal property of the composites also significantly enhanced in the presence of small amount of graphite nanosheets.

#### **HDPE/graphene composites**

Zheng et al. [262] have worked on HDPE/EG composite, prepared by melt compounding process. They observed that viscosity of the pure polymer is increased with the incorporation of the EG nanofillers in the composite due to increase the surface to volume ratio for EG nanofillers. The EG acted as nucleating agent to induce crystallization of HDPE in the composite. However, the degree of crystallinity of HDPE decreased with increasing the nanofiller loading in the composite which indicated that the sizes of crystallites and crystalline phase decreased in the presence of in homogeneities. The electrical conductivity, mechanical strength and stiffness of HDPE increased with the incorporation of EG in the polymer matrix. The EG act as a reinforcement materials which restricted the chain mobility of the matrix polymer and increased the mechanical strength of the pure polymer.

#### **PVDF/graphene composites**

Poly(vinylidene fluoride) (PVDF)/functionalized graphene sheets (FGS) composite was prepared through solution method followed by compression molding [169]. The thermal stability and the mechanical property of the composite were very high compared to pure PVDF. The storage modulus of neat PVDF was greatly increased with the incorporation of the FGS. These composite materials can be used as positive temperature coefficient (PTC) materials and conductive materials because the resistivity changes at higher nanofiller loadings.

**Table 3** summarizes the electrical conductivity of polymer/graphene composites. The electrical conductivity of the composites depends on the processing method, polymer matrix and nanofiller type.

**Table 3.**The Electrical Conductivity of different polymer/graphene composites

Polymer	Graphene Type	Method	Conductivity (S m <sup>-1</sup> )	Loading (wt%)	References
epoxy	RGO	ball mill process	$\sim 1.47 \times 10^{-8}$	0.2	[403]
epoxy	EG	Ultra-sonication	$\sim 1.0 \times 10^{-4}$	3	[389]
epoxy	EG	Solution mixing	$\sim 1.0 \times 10^{-2}$	2.5 v/o%	[392]
epoxy	Graphene	Solution mixing	$\sim 1.0 \times 10^{-2}$	0.52 vol%	[393]
WPU	S-GNS	Solution mixing	$\sim 5.1 \times 10^0$	7.7	[404]
PEDOT	Graphene	<i>In-situ</i>	$\sim 3.5 \times 10^1$	15.1	[405]
PMMA	Graphene-13.2	Solution blending	$\sim 10^1$	2.67 vol%	[394]
PMMA	EG	Solution mixing	$\sim 1.0 \times 10^{-3}$	1	[256]
PMMA	EG	<i>In-situ</i>	$\sim 7.76 \times 10^1$	10	[249]
PMMA	NanoG	<i>In-situ</i>	$\sim 1.0 \times 10^{-3}$	0.68 vol%	[406]
UHMWPE	Graphene	Melt mixing	$\sim 1.0$	0.2 vol%	[407]
HDPE	EG	Melt mixing	$\sim 1.0 \times 10^{-8}$	3	[262]
HDPE	UG	Melt mixing	$\sim 1.0 \times 10^{-10}$	5	[262]

PS	Functionalized graphene	Melt mixing	$\sim 4.6 \times 10^{-1}$	0.96 vol%	[395]
PS	EG	<i>In-situ</i>	$\sim 1.0 \times 10^{-4}$	1.5 vol%	[396]
PS	Graphene	<i>In-situ</i>	$\sim 1.0 \times 10^{-2}$	2	[248]
PS	Graphene	Solution mixing	$\sim 2.4 \times 10^1$		[391]
PS	Graphene	Solution mixing	$\sim 1.0 \times 10^{-5}$	0.1 vol%	[257]
PS	GNS <sup>C4P</sup>	Solution mixing	$\sim 4.0$	0.1 vol%	[195]
PS	NanoG	<i>In-situ</i>	$\sim 1.0 \times 10^{-4}$	1	[408]
PC	GO	microwave-exfoliation	$\sim 2.5 \times 10^{-1}$	3	[390]
PC	graphite	Melt mixing	$\sim 6.6 \times 10^{-11}$	12	[397]
PC	FGS		$\sim 1.0 \times 10^{-9}$	2	
PVA	RGO		$\sim 8.9 \times 10^{-1}$	3	[409]
PVA	RGO	Solution blending	$\sim 8.9 \times 10^{-3}$	3	[398]
PVA-S	NanoG	Solution mixing	$\sim 1.0 \times 10^{-3}$	0.2	[410]
PET	Graphene		$\sim 7.4$	2.4 vol%	[411]
Chitosan	graphene sulphonic acid	Solution blending	$\sim 1.3 \times 10^{-1}$	1.6	[412]
PI	Graphene	<i>In-situ</i>	$\sim 8.9 \times 10^{-5}$	0.75	[250]
PET	Graphene	melt compounding	$\sim 2.11$	3 vol%	[399]
PET	Graphene	Melt mixing	$\sim 7.4 \times 10^{-2}$	0.47	[261]
Nylon 6	EG	<i>In-situ</i>	$\sim 1.0 \times 10^{-1}$	1.5 vol%	[252]
Nylon 6	FG	<i>In-situ</i>	$\sim 1.0 \times 10^{-5}$	0.75 vol%	[400]
PA 6	GO	<i>In-situ</i> polymerization	$\sim 2.8 \times 10^{-2}$	$\sim 1.64$ vol%	[413]
PLA	Glucose reduced RGO	Solution blending	$\sim 2.2$	$\sim 1.25$ vol%	[414]
PPS	EG	Melt mixing	$\sim 1.0 \times 10^{-3}$	4	[401]
PPS	S-EG		$\sim 1.0 \times 10^{-2}$		
Isotactic PP	GNS	<i>In-situ</i> polymerization	$\sim 1.2 \times 10^{-8}$	8.2	[415]
PVDF	EG	Solution mixing	$\sim 1.0 \times 10^{-3}$	5	[169]
PVDF	FGS	Solution mixing	$\sim 1.0 \times 10^{-2}$	2	
PANI	Graphite	<i>In-situ</i> polymerization	$\sim 3.3 \times 10^3$	1.5	[402]

### Supercapacitor

In definition, supercapacitor is high capacity electrochemical capacitor that makes a bridge among electrolytic capacitor and rechargeable batteries. They typically store 10 or 100 times more energy per unit volume or mass than electrolytic capacitors, can accept and deliver charge much faster than batteries and tolerate many more charge-discharge cycles than rechargeable batteries. Thus, supercapacitor has gained enormous interest in current science for energy storage devices. Due to their rapid charging-discharging rates, high power density and long cycle life (>100000 cycles), it has huge applications in various fields of electronics [416,417]. In addition, it has been considered alternative energy sources for electric vehicles and digital communication devices in modern time [418]. Thus, it has been considered as key material for next generation energy sources in all electric cars and cars based on fuel cells like direct methanol fuel cell (DMFC), hydrogen fuel cell [419], etc.

For the preparation of supercapacitor materials, transition metals oxides have taken part an important role along with graphene or conducting polymer, known as

pseudocapacitance [420]. RuO<sub>2</sub> is very useful material for redox transitions. However, it is very costly. Recently, preparation of cost-effective electrode materials with a high capacitance value becomes challenging. In this regard, various cheap metal oxides (oxides or salts of Ni, Co, In, Sn, Fe, Mn) and conducting polymers [PANI, PPY, PTH and their derivatives] are widely used along with conducting nanofillers. Supercapacitor based on PANI has been reported widely due to its easy synthesis procedure, redox reversibility, good environmental stability, high electrical conductivity and obviously its low cost [421]. CNTs and graphene and their derivatives have been considered most promising nanofillers for supercapacitor applications.

Li et al. [422] have studied the capacitance value of PANI/graphene nanosheet composite at various scan rates. The obtained capacitance value was  $\sim 1130$  F/g at 5 mV/s scan rate. They used *in-situ* polymerization of aniline in the presence of graphene nanosheet for the preparation of composite. Wang et al. [423] have used flexible graphene for the preparation of PANI/flexible graphene hybrid materials. They achieved high specific capacitance value of  $\sim 1126$  F/g. they observed that

flexible graphene shows high capacitance value compared to normal graphene sheet. Yan et al. [424] have prepared PANI/graphene nanosheet as electrode for supercapacitor material through *in-situ* polymerization of aniline in the presence of graphene nanosheet. They have measured the capacitance value of the composite and achieved value of  $\sim 1046$  F/g at 1 mV/s scan rate. Zhang et al. [425] have reported specific capacitance value of  $\sim 480$  F/g at a current density of 0.1 A/g for PANI/graphene composite. They also used *in-situ* polymerization method for the preparation of composite. Liu et al. [426] have synthesized PANI/flexible graphene sheet composite for supercapacitor application. They have studied specific capacitance of the composite and observed value was  $\sim 301$  F/g. Wang et al. [427] have used PANI and flexible graphene for the preparation of supercapacitor electrode. They have studied gravimetric capacitance ( $\sim 233$  F/g) and volumetric capacitance ( $\sim 135$  F/cm<sup>3</sup>) of the composite. Khatua et al. [428] have used metal salt for the preparation of PANI/GNP/CoCl<sub>2</sub> composite through *in-situ* polymerization method. The reported specific capacitance value was  $\sim 635$  F/g at 10 mV/s scan rate. Sahoo et al. [429] have synthesized PPY/graphene composite through *in-situ* polymerization. They have measured capacitance value of the composite and obtained value was  $\sim 466$  F/g at 10 mV/s scan rate. They have described how anions and cations are moved in electrochemical double layer system during charge/discharge mechanism and represented schematically in Fig. 15. They also reported that composites is highly electrically conductive in nature and behaves like semiconductor.

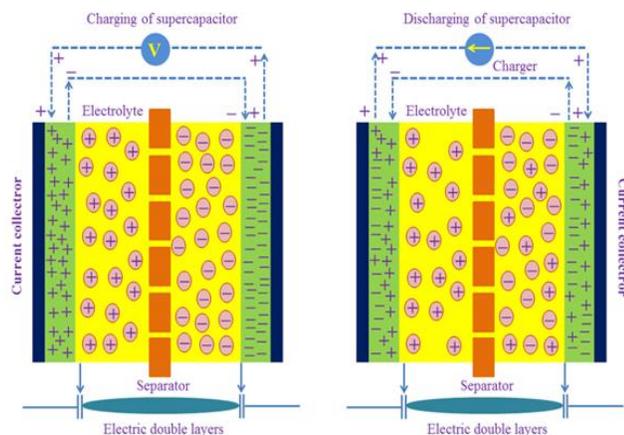


Fig. 15. Schematic representation of the movements of ions in electrochemical double layer type capacitor during charging/discharging.

### Classifications of supercapacitor

Generally, supercapacitors can be classified into three main classes, such as (a) electrochemical double layer capacitors (EDLCs), (b) pseudocapacitors, and (c) hybrid capacitors [430]. The classification has been done based on its unique charge storage mechanism which may be Faradaic, non-Faradaic and a combination of the two,

respectively. For Faradaic charge storage process, oxidation-reduction reactions involve the charge transfer that observed between electrolyte and electrode. In non-Faradaic mechanism, charges are distributed on surfaces through physical processes which do not involve in making or breaking of chemical bonds.

### Electrochemical double-layer capacitors

For EDLCs, the capacitance value obtained due to charge separation at the electrode-electrolyte interface. The non-faradic type charge storage mechanism is observed for EDLCs where carbon-based nanofillers are extensively used for developing electrical charge at the electrode-electrolyte interface. Although EDLCs have high power density, but suffers from low capacitance and low rate capability. For EDLCs, charge store is electrostatically or non-Faradaically (for carbon based nanofillers) and charge transfer does not observed between electrode and electrolyte. EDLCs use an electrochemical double-layer charge for energy storage. When the voltage is applied, charge accumulates around the surfaces of the electrodes. The natural attraction of unlike charges, solvated ions in the electrolyte solution diffuse across the separator into the pores of the electrodes of opposite charges. The design of working electrode (cathode) and counter electrode (anode) are well proposed to avoid the recombination of the solvated ions. Thus, a double-layer of charge can be stored at the electrode surfaces (working and counter electrodes). Thus, produced double-layers increase the surface area of electrode and reduce the distance between electrodes, help to increase the energy densities of EDLCs than conventional capacitors. In the case of non-Faradaic processes, chemical or composition changes are not occurred as charge transfer is not happened between electrode and electrolyte. Due to this mechanism, charge storage in EDLCs is highly reversible with very high cycling stabilities. In general, EDLCs operate with stable performance for many charge/discharge (CD) cycles. EDLCs are suitable for the applications in non-user serviceable locations such as mountain environments or deep sea due to their cycling stability. The performance of EDLCs depends on the nature of its electrolyte. EDLCs can be used either an aqueous or organic electrolyte. Aqueous electrolytes such as H<sub>2</sub>SO<sub>4</sub> and KOH which have lower equivalent series resistance (ESR) and lower minimum pore size requirements compared to organic electrolytes. However, the major problem of aqueous electrolytes is that it has lower range of breakdown voltages. Therefore, one must consider the tradeoffs between capacitance, ESR, and voltage in choosing between an aqueous or organic electrolyte [431,432]. The nature of the electrolyte takes part great role to design the supercapacitor. Carbon electrode materials generally have higher surface area, lower cost, and more established fabrication techniques than other materials, such as conducting polymers and metal oxides. Different carbon nanomaterials can be used to store charge in EDLC electrodes such as activated carbons, carbon aerogels, CNTs and graphene.

### *Pseudocapacitors*

The pseudocapacitor is one of the classifications of supercapacitor, utilize fast and reversible surface or near surface reactions for charge storage. For pseudocapacitors, various metal oxides or salts ( $MO_n$ ,  $MX_m$  etc) or conducting polymers are used as electrode materials. For it, charge transfer was observed between electrolyte and electrode at the electrode-electrolyte interface through Faradic charge transfer mechanism. It is completed through electrosorption, reduction-oxidation reactions, and intercalation processes [433,434]. Pseudocapacitor is more useful as capacitor material compare to EDLCs [433]. The pseudocapacitors are two types, one is metal oxides or salts based and other is conducting polymers based pseudocapacitors.

#### *Metal oxides or its salts*

Various metal oxides or its salts are extensively used along with nanofillers to enhance the capacitance value of the materials and help to increase its application areas [435,436]. Generally,  $RuO_2$  shows high capacitance value compared to others, but it is very costly. Recently, different cheap metal oxides or its salts ( $MO_n$ ,  $MX_m$  etc) are extensively using to get high capacitance value and make it industrially feasible.

#### *Conducting polymers*

Conducting polymers such as PANI, PPY etc are one of the components along with nanofillers to prepare the high performance capacitor materials. These polymers are comparatively cheap and easily available [433]. The n/p-type polymers with negatively charged (n-doped) and positively charged (p-doped) shows highest potential energy and power densities and more applicable in various fields.

#### *Hybrid supercapacitors*

In hybrid supercapacitors, both Faradaic and non-Faradaic processes are involved for charge storage. It is more fruitful compared to EDLCs [437] and pseudocapacitors. Generally, it is three types, such as (i) composite capacitor, (ii) asymmetric capacitor, and (iii) battery-type capacitor, respectively.

#### *Composite capacitor*

Composite electrodes are the combination of carbon-based nanofillers with either conductive polymer or metal oxide. Here, both chemical and physical charge storage mechanisms are involved together in a single electrode. The high-surface-area of nanofillers facilitates capacitive

double-layer charge [433] by increasing the contact area among electrolyte and deposited pseudocapacitive materials. Due to Faradic charge transfer mechanism, high capacitance value was observed [438]. The PPY/RGO composite are very useful supercapacitor material which shows higher capacitance value compared to pure RGO or pure PPY [439, 440].

#### *Asymmetric capacitor*

Asymmetric capacitor is the combination of Faradaic and non-Faradaic processes which is prepared by coupling an EDLC electrode with a pseudocapacitor electrode. The negative electrode of activated carbon coupled with positive electrode of conducting polymer to prepare the asymmetric capacitor and make it more applicable [433, 441]. Asymmetric hybrid supercapacitors have higher energy, power densities and better cycling stability.

#### *Battery-type capacitor*

The battery type capacitor can store more energy compared to others and it shows very high capacitance value. Research has focused primarily on using  $Ni(OH)_2$ ,  $PbO_2$ , and LTO ( $Li_4Ti_5O_{12}$ ) as one electrode and activated carbon as the other [442,443] for the preparation of high performance battery type capacitor. Although there is less experimental data on battery type hybrids than on other types of supercapacitors. The available data suggest that these hybrids may be able to bridge a gap between supercapacitors and batteries. Despite the promising results, the general consensus is that more research will be necessary to determine the full potential of battery-type hybrids.

#### *CNT based supercapacitor*

CNTs are extensively used as conducting nanofiller for the preparation of supercapacitor materials in different composite systems. CNTs have been much attracted as supercapacitor electrode materials due to their unique mesoporous network, high electrical conductivity, outstanding electrochemically accessible surface area and very high chemical stability. In addition, CNTs provide high electrically conducting network structure in the composites to facilitate a fast electrochemically kinetic process during charge/discharge mechanism. To improve the electrochemical value, CNTs are decorated with different metal oxides, conducting polymers. Thus, different types of CNT based composites were prepared to increase the specific capacitance value of the composites using metal oxides and conducting polymer. The specific capacitance value at different scan rate of various CNT based composites are summarized in **Table 4**.

**Table 4.** Specific capacitance value of different CNT based composites.

Composition	CNT Type	Preparation Method	Specific Capacitance	Current density/Scan rate	References
$Ni(OH)_2$	MWCNT	Successive ionic layer adsorption and reaction method	~1487 F/g	5 mV/s	[444]
polymer-modified graphene sheets	Acid-oxidized MWCNT	<i>In-situ</i> reduction of exfoliated graphite oxides	~120 F/g	1 V/s	[445]

vertically aligned CNTs on conductive carbon papers via water-assisted chemical vapor deposition	RuO <sub>2</sub>	CNT	in the presence of cationic poly(ethyleneimine) solution-based method	~953 F/g	1 mV/s	[446]
	vanadium nitride	Vertically aligned CNT	water-assisted chemical vapor deposition	~200 F/g	20 A/g	[447]
Molybdenum oxide	MWCNT	MWCNT	Inconel electrodes	~289 F/g	20 mV/s	[448]
	MWCNT	MWCNT	DC reactive magnetron sputtering of molybdenum	~70 F/g	10 mV/s	[449]
3D N-doped graphene	CNT	CNT	hydrothermal treatment	~180 F/g	0.5 A/g	[450]
functional carbon nanotube-mesoporous carbon (CNT-MC) networks via facile organic sol-gel chemical route	Functional mesoporous carbon-coated CNT	Functional mesoporous carbon-coated CNT	Sol-gel chemical route, and freeze-dried followed with pyrolysis	~214 F/g	10 mV/s	[451]
TPU/CuFe <sub>10</sub> Al <sub>2</sub> O <sub>19</sub>	MWCNT	MWCNT	<i>In-situ</i> synthesis	~269 F/g	10mV/s	[452]
Ni(OH) <sub>2</sub>	Polypyrrole-derived CNT	Polypyrrole-derived CNT	Facile synthesis	~1118 F/g	50 mA/ cm <sup>2</sup>	[453]
∞-MnOOH coaxial nanocable	MWCNT	MWCNT	electrophoretic deposition process	~202 F/g	~0.65 A/g	[454]
MoO <sub>3</sub>	MWCNT	MWCNT	Sonochemical method	~103 F/g	25A/g	[455]
NiO	MWCNT	MWCNT	Sonochemical method	~328 F/g	0.33 A/g	[456]

### Graphene based supercapacitor

In the recent time, graphene has been widely used as most promising nanofillers for the preparation of supercapacitor electrode materials due to their single atom thick, two dimensional sheet of sp<sup>2</sup>-hybridized carbon atoms arranged in a honeycomb crystal structure with exceptionally high strength, high electrical conductivity, high surface area, thermal conductivity and unique mesoporous network. The superior electron mobility of platelet likes graphene facilitates the electron propagation

during the charge/discharge mechanism and enhances capacitance value of the composites. However, the capacitance value of graphene is low and graphene is very costly. So, graphene is decorated with different conducting polymers and metal oxides to enhance the electrochemical properties of the composites and reduce the cost of the electrode materials. Thus, different types of graphene based composites were prepared to increase the specific capacitance value of the composites using metal oxides and conducting polymer as shown in **Table 5**.

**Table 5.** Specific capacitance value of different graphene based composites.

Composition	Graphene Type	Method	Specific Capacitance	Current density/Scan rate	References
Ni(OH) <sub>2</sub>	ultrathin-graphite foam	hydrothermal reaction	~111 F/g	10 A/g	[457]
PPY	functionalized graphene sheets	Interfacial/ <i>In-situ</i> oxidative polymerization	~277.8 F/g	10 mV/s	[458]
Ultrathin MnO <sub>2</sub>	graphene nanosheets.	Solution mixing	~208 F/g	10 A/g	[459]
ultrathin MnO <sub>2</sub> sheet	Nitrogen-doped graphene	hydrothermal method	~192.5 F/g	2 A/g	[460]

PANI hollow spheres	electrochemical RGO	solution-based coassembly process	~614 F/g	1 A/g	[461]
PANI	Graphene	<i>In-situ</i> polymerization	~257 F/g	0.1 A/g	[462]
titanium dioxide	graphene	hydrothermal approach	~107.0 F/g	10 A/g	[463]
PANI	graphene nanoribbons	<i>In-situ</i> polymerization	~257 F/g	4 A/g	[464]
A Ni-Al layered double hydroxide/mutil-wall carbon nanotube	RGO sheet	solvothral method	~1404 F/g	5 mV/s	[465]
	Crumpled graphene balls	aerosol spray drying process followed by reduction	~150 F/g	0.1 A/g	[466]
MnO <sub>2</sub>	Graphene	Electrochemical deposition	~130 F/g	2 mV/s	[467]
PANI nanowafer	partially reduced graphene oxide nanosheet	<i>In-situ</i> polymerization method	~329.5 F/g	5 mA/cm <sup>2</sup>	[468]
PANI nanorods	expanded graphite nanosheets	<i>In-situ</i> polymerization	~1665 F/g	1 A/g	[469]
needle-like nano-MnO <sub>2</sub>	graphene	Solution mixing	~124 F/g	200 mA/g	[470]
PANI	GO	<i>In-situ</i> polymerization with the assistance of supercritical carbon dioxide (SC CO <sub>2</sub> )	~425 F/g	0.2A/g	[471]
Ni(OH) <sub>2</sub>	RGO	electrophoretic deposition	~1404 F/g	2A/g	[472]
PANI -graphene hybrid connected by amide groups	graphene	<i>In-situ</i> polymerization	~623.1 F/g	0.3 A/g	[473]
Thermally treated reduced graphite oxide	RGO	Thermal treatment in nitrogen atmosphere	~96 F/g	5 mV/s	[474]
sulfonated poly (ether-ether-ketone)	graphene	<i>In-situ</i> polymerization followed by reduction	~476 F/g	6.6 A/g	[475]
PANI	Amide modified graphene	Solution casting	~361.9 F/g	1 A/g	[476]
PANI	amine-modified RGO	<i>In-situ</i> chemical oxidative polymerization of aniline	~388 F/g	1 A/g	[477]
Nano-size MnO <sub>2</sub>	activated microwave expanded graphite oxide	Self-controlled redox deposition process	~850 F/g	0.25 A/g	[478]
MnO <sub>2</sub>	Embossed-chemically modified graphene	using polystyrene colloidal particles as sacrificial templates	~389 F/g	1 A/g	[479]
Mn <sub>3</sub> O <sub>4</sub>	Graphene	hydrothermal process	~115 F/g	1 A/g	[480]

Co <sub>3</sub> O <sub>4</sub>	three-dimensional graphene	<i>In-situ</i> synthesized	~1100 F/g	10 A/g	[481]
PANI PPY	RGO	<i>In-situ</i> polymerization process	~361 F/g	0.3 A/g	[482]
PEDOT			~248 F/g		
			~108 F/g		
Ni(OH) <sub>2</sub>	graphene	prepared based on a solid state reaction	~1568 F/g	4 A/g	[483]
graphene hydrogels	Hydrazine reduced graphene hydrogels	Hydrothermal process	~222 F/g	1 A/g	[484]
Ni <sup>2+</sup> /Al <sup>3+</sup> layered double-hydroxide	graphene nanosheet	hydrothermal method	~781.5 F/g	5 mV/s	[485]
	functionalized graphene	Solvothermal method	~276 F/g	0.1 A/g	[486]
MnO <sub>2</sub>	Functionalized graphene	Electrostatic coprecipitation method	~142 F/g	2 A/g	[487]
PANI	functionalized hydrogen-exfoliated graphene sheets	Poly condensation method	~375 F/g	10 mV/s	[488]
ZnO	RGO	Solvothermal treatment in air	~308 F/g	1 A/g	[489]
PPY	sulfonated graphene	Electrochemical polymerization	~285 F/g	0.5 A/g	[490]
PPY Nanowires	Graphene Nanosheets	<i>In-situ</i> polymerization process	~165 F/g	1 A/g	[491]
PANI nanofibers	chemically converted graphene	vacuum filtration	~210 F/g	0.3 A/g	[492]
PANI	Chemically modified graphene	<i>In-situ</i> polymerization	~480 F/g	0.1 A/g	[493]
MnO <sub>2</sub>	Graphene nanoribbons	solution-based oxidative process	~266 F/g	1 A/g	[494]
porous nanorod-PANI	graphene	<i>In-situ</i> electrochemical polymerization	~878.57 F/g	1 A/g	[495]
PANI nanofibers	graphene nanosheets	<i>In-situ</i> polymerization	~1130 F/g	5 mV/s	[496]
PANI	flexible graphene	<i>In-situ</i> polymerization–reduction/dedoping–redoping process	~1126 F/g		[497]
PANI	graphene nanosheet	<i>In-situ</i> polymerization	~1046 F/g	1 mV/s	[498]
PANI	graphene	<i>In-situ</i> polymerization	~480 F/g	0.1 A/g	[499]
PANI	flexible graphene	<i>In-situ</i> electro-polymerization method	~233 F/g		[500]
PANI nanofiber	graphene		~210 F/g	0.3 A/g	[492]
PPY	graphene	<i>In-situ</i> polymerization	~466 F/g	10 mV/s	[429]
PANI	Graphene	Electrochemical polymerization	~210 F/g	0.3 A/g	[501]

PPY	GO	in situ chemical polymerization	~728 F/g	0.5 A/g	[502]
MnO <sub>2</sub> /PANI	sulfonated graphene	<i>In-situ</i> polymerization	~276 F/g	1A/g	[503]
SnO <sub>2</sub>	Graphene nanosheets	hydrothermal reduction	~368 F/g	5mA cm <sup>-2</sup>	[504]
nitrogen-modified few-layer graphene	graphene	Ultra-sonication followed by annealing process	~227 F/g	1A/g	[505]
Poly (3-hexylthiophene)	graphene	<i>In-situ</i> growth technique	~323 F/g	200 mA/g	[506]
MnO <sub>2</sub>	Graphene	chemical reduction of GO/MnO <sub>2</sub> using hydrazine hydrate	~327.5 F/g	10 mV/s	[507]
Co <sub>3</sub> O <sub>4</sub> nanoparticles	RGO	hydrothermal processing	~472 F/g	2mV/s	[508]
Mn <sub>3</sub> O <sub>4</sub>	GO	ionic layer adsorption and reaction (SILAR) method	~344 F/g	5 mV/s	[509]
RGO paper	GO paper	flame-induced reduction in KOH aqueous solution	~212 F/g	1 A/g	[510]
graphene-beaded carbon nanofibers	carbon nanofibers	electrospinning	~263.7 F/g	100 mA/g	[511]
Carbon nanohorn	GNP	Solution mixing	~677 F/g	10 mV/s	[512]
PANI	Carbon nanohorn	<i>In-situ</i>	~834 F/g	5 mV/s	[513]
PANI/Zinc acetate	GNP	<i>In-situ</i>	~670 F/g	1.85 A/g	[514]

## Conclusion

In summary, we have focused the electrical and electrochemical properties of the composites based on CNTs, graphene and their functionalized derivatives. In the recent time, CNTs and graphene have been attracted in various fields and turn the scientific research, especially nano science in new direction. These nanofillers are extremely used in the field of different applications such as electromechanical actuators, composite materials, nano-electronic and photovoltaic devices, superconductors, aerospace. nanowires, Li-ion batteries, EMI shielding materials, supercapacitor, actuators, antistatic materials, electro-active materials, pressure sensors, ESD coatings, percolative conducting polymer composites and as charge-storage capacitors etc. Due to nano-sized, high aspect ratio, high surface area and extremely high electrical conductivity, insulating polymers become conducting in the presence of small amount of nanofiller and properties (such as electrical, mechanical and thermal) of the insulating polymer tremendously changed. Thus, polymer/nanofiller composites have been extensively used in the various fields with wide applications. The major drawback is the homogeneous and regular dispersion of the nanofillers throughout the matrix. Several studies have been going on for homogeneous dispersion of the nanofillers throughout

the matrix polymer to reduce the nanofiller loading as well as improve the properties of the matrix polymer. To improve the better dispersion of the nanofillers, several methods have been developed such as solution blending, *in-situ* polymerization and melt blending. The dispersion of the nanofillers has been improved through different functionalization of the nanofillers which is reported by several groups. The properties of the polymer/functionalized nanofiller composites also increased due to functionalization of the nanofillers.

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