The University of Nottingham Malaysia Campus

Faculty of Engineering

Department of Mechanical, Materials and Manufacturing Engineering

Preparation, characterisation and applications: Boron nitride nanotubes (BNNTs), BNNTs-graphenehybrid and their polymer nanocomposites

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Abstract

Boron nitride nanotubes (BNNTs) are unique one-dimensional crystal structures exfoliated from boron nitride (BN). In recent years, BNNTs have drawn attention because of their exceptional properties. The physicochemical properties including thermal and electrical insulation, high repulsion to water molecules, acid resistance, high hydrogen storage capacity and mechanically robust as graphene. There are various methods for the preparation of BNNTs such as top-down, bottom-up, chemical vapour deposition and co-precipitation process. Among that, large-scale production of BNNTs by using co-precipitation method is a promising way for industrialisation. In this work, the synthesis of BNNTswasachieved by co-precipitation and annealing route using amorphous boron, ferric nitrate nanohydrate ($Fe(NO_3)_3.9H_2O$ and urea ($CO(NH_2)_2$) as the raw materials. The BNNTs were later combined with graphene to produce novel hybrid structure through liquid-phase exfoliation method. Graphene was produced through Hummer's method followed by reduction and purification process.

Two types of polymer nanocomposites were prepared by using solvent mixing method. (a) BNNTs incorporated with polycaprolactone (PCL) to investigate the mechanical and thermal properties and (b) Graphene reinforced with polylactic acid (PLA) to study the toxicity of the nanocomposite.The polymer nanocomposite of BNNT reinforced with PCL were characterizedby using scanning electron microscope (SEM), thermal gravimetric analysis (TGA), X-ray diffraction (XRD), UV-visible spectrometer and tensile test. The tensile strength was increased by 101 % for PCL incoprated with 5 wt% of BNNTs compared to the pure PCL. However, in thermal analysis PCL-2BNNTs and PCL-5BNNTs showed thesame decomposition compared to pure PCL. There were 1 % to 4 % residues of PCL-2BNNTs and PCL-5BNNTs due to thepresence of BNNTs. The biocompatibility of PLA-graphene was tested by using *Caenorhabditiselegans (C. elegans)*.

The PLA-graphene did not show any negative effects andoutcomehas no cause of toxicity on the human organism. As a result, it was determined that the polymer nanocomposites are applicable in mechanical and biomedical applications.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter 1
Introduction

1.1 Background

In recent decades, the significant research has been dedicated to the studies on polymer nanocomposites. To a great extent, composites based on polymeric materials have been an area of interest in both academics as well as in industry. Polymer nanocomposite is a combination of two or more components, one with the stiff and strongnanoparticles (fillers) and other which is a polymer (matrix). When the filler and matrix are combined, the resulting polymer nanocomposite material will keep the individual characteristics (both filler and matrix) and both directly influence the prepared final composite properties. The further improvement in the physical and chemical properties depends on the interaction or cooperation between the inorganic and organic compounds. The enhanced properties play a vital role in developing advanced functional materials for many emerging applications in the field of mechanical, electrical and biomedical.

A number of carbon based materials of various forms, such as carbon nanotubes (CNTs), graphene and its derivatives, buckminsterfullerene (fullerene), carbon black (CB) has been combined with various polymer matrices. Apart from carbon based materials, boron nitride which regarded structurally analogous to carbon lattice has been incorporated into different polymers matrix. Both types of composite materials have been investigated in the enhancements of physiochemical properties. The changes in various properties by customising chemical interactions with polymer matrices, exclusively in carbon based and boron nitride materials have not been explored thoroughly. Besides, it remains a space for developing biodegradable and low-cost polymer nanocomposites that could further encourage the

production of large quantities of standardised products and steer extensive commercialisation. These features are mainly evaluative or else substituting the existing materials in applications will not become a reality.

1.2 Problem statement

Polymer nanocomposites reinforced with synthetic nanofillers continue to accomplish the worldwide demand for substitute materials with low cost and better physicochemical properties. In current years, BNNTs and graphene have emerged as subjects of enormous scientific interest and have magnetised a considerable deal of recognition across several fields ranging from electromechanical devices to biomedical. The materials are found their way into applications such as solar cells, electronic circuits, tissue engineering and drug delivery. Individually, graphene and BNNTs showed different characteristics. However, considering graphene, it has higher surface area compared to BNNTs. In contrast, BNNTs are an excellent electrical insulator with higher band gap. The layered BN structure is much more thermally and chemically stable than a graphitic carbon structure. Therefore, both as fillers for polymers are able to enhance physicochemicalproperties. Also, it is anticipated that hybrid nanostructure which isformed of graphene and BNNTs will show very exceptional characteristics.

An increasing number of nanomaterials and polymer nanocomposites hasbeen developedfor diverse biomedical applications. Among these materials, graphene has been studied for drug delivery and tissue engineering. Hence it is essential to identify the toxicity of materials before utilising in the biomedical products.

1.3 Aim and objectives

The aim of the study was to synthesise and to characterizethe BNNTs-graphene hybrid and their polymer nanocomposites

Below are the objectives of research:

- To synthesise, optimise and characterise the BNNTs, graphene and nanohybrid (BNNTs-graphene).
- To evaluate the surface morphological, mechanical and thermal properties of PCL reinforced with BNNTs.
- To assess the toxicity of the graphene and PLA-graphene nanocomposite with a tool of microorganism *C. elegans* and suggest the biocompatibility.

1.4 Thesis outline

This thesis contains seven chapters. The draft of chapters are as follows:

Chapter 1 focusedon the background study, the problem statement, aim and objectives and chapter outline of this thesis.

Chapter 2 discussed about the intensive literature review on polymer nanocomposites and polymer nanocomposites preparation methods. As well as about graphene and BNNTs synthesis, properties and applications. Furthermore, the biocompatibility of nanocomposites and evaluation of nanocomposites using *C. elegans*was described.

Chapter 3explained materials and methodology incorporated in performing the experimental work of this study. The synthesis of nanofillers and preparation of nanocomposites were included in this chapter. Additionally, a detailed list of characterisation such as structural, mechanical, thermal properties and in-vitro analysis of nanocomposites havebeen reported.

Chapter 4 inscribed the results and discussion for synthesised nanofillers and nanohybrid.

Chapter 5 explained the characterisation of PCL-BNNTs polymer nanocomposite.

Chapter 6describedthe toxicity analysis of the graphene and PLA-graphene nanocomposite by using *C. elegans*.

Chapter 7 discussed the conclusion and proposed future scope based on the aims and objectives of the present study.

Chapter 2

Literature review

2.1 General background on polymer nanocomposites

Polymer nanocomposites havebeen developed by incorporatingnanofillers into thepolymer matrix. The nanofillersare typically used to improve specific properties of polymers [1]. The nanocomposites based on synthetic nanofillershave gained attention because of their capability to enhance mechanical [2–4], thermal [5, 6] and electrical [7–9] properties of polymers. Polymer nanocomposites havebeen presented with synthetic nanofillersat lesser or same loadings to have properties that are identical or superior to those of polymer composites with traditional fillers[10, 11]. The homogenous dispersion of nanofillerin polymer matrix is desired. Figure 1 presented various types of nanofillers. It can be a challenge to produce an approving interaction between the polymer and the nanofiller. The polymer nanocomposites with synthetic fillershave been applicable in abroad range of areas such as conductivity [12] melt processing [13], moisture barrier [14] and photo-catalyst activation [15]. The large interfacial phase between filler and matrix possess thermodynamic stability, which contributes to enrichingthe physical properties of the polymer nanocomposite [16].

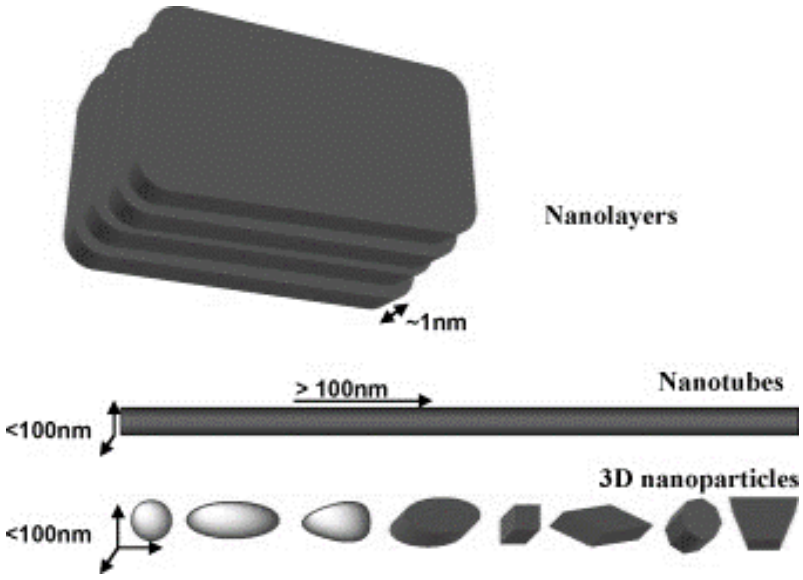


Figure 1 Various types of nanofillers[17].

2.1.1 Preparation of polymer nanocomposites

The nature of bonding interaction plays a crucial role in the interface between the matrix and filler, which has significant developments in the properties of the prepared polymer nanocomposite. Most of the composites are prepared by using a non-covalent or covalent processes where the polymer matrix and the filler react with each other to promote stronger interfacial bonding, as will be explained in the following sections. Figure 2 shows the schematic illustration of polymer composite preparation using two types of bonding methods.

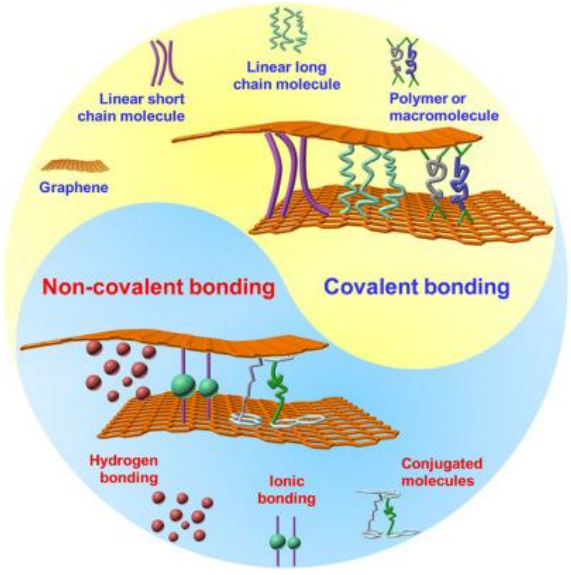


Figure 2 Schematic illustration of non-covalent bonding and covalent bonding[18].

2.1.1.1 Non-Covalent dispersion

Non-Covalent functionalisation is a well-known technique for mixing the filler with polymer matrix through weak van der Waals and electrostatic forces. Non-covalent dispersion is typically classified into two methods, namely solution mixingandmelt mixing.

The solution mixing is the most straightforward method to produce the polymer nanocomposites. The process as shown in Figure 3 involves in three principal steps. Firstly, the filler dispersion in an appropriate solvent using for an instanceultrasonication. Secondly, theinclusion of the polymer and finally, washing the solvent by filtration or evaporation [15, 19]. Otherwise, the solvent can be removed by casting the suspension of filler and polymer in a mold. The graphene was incorporated into different types of polymers including polycarbonate, polyacrylamide, polyimides and poly (methyl methacrylate), polystyrene [20–24]through this method. Furthermore, it showed fascinating results with a water-soluble polymer like polyvinyl alcohol (PVA) and poly(allylamine) composites [25–32]. Few other methods like phase transportation, lyophilisation, surfactants engaged with solution mixing but surfactants methodexhibit some defects in compositesfor example increase the thermal resistance in thematrix and filler interfacial, diminishing the thermal conductivity of filler [33]. Solution mixing method must be used with carefulness, as re-aggregation of the sheets regularly happens through evaporation. It is significant to find ways to functionalized the nanofillers to avoid aggregation by accumulating the solubility of nanoparticles in similar solutions.

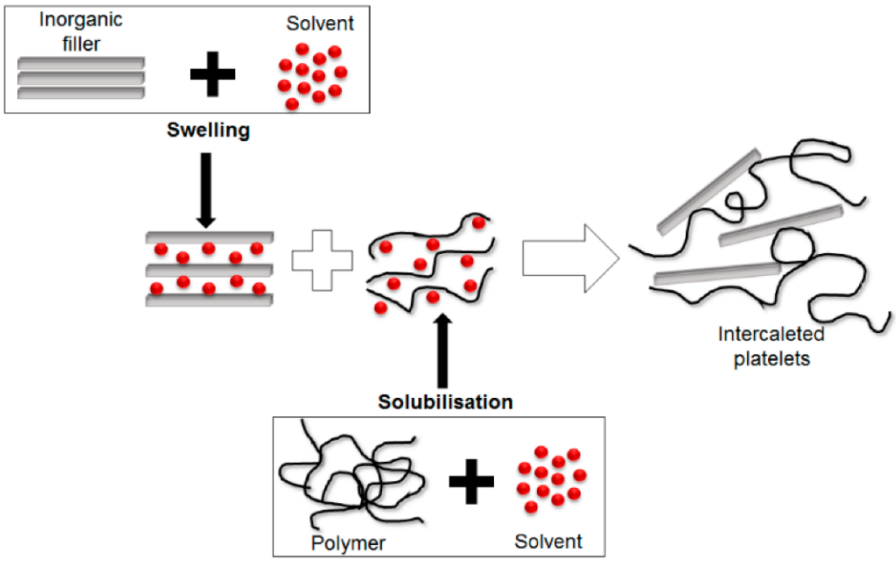


Figure 3 Schematic representation of the solvent mixing processing [34].

The second technique in thenon-covalent dispersion is melt mixing method. The process includes a polymer and filler in dried powder form. The dried powder was mixed by utilising melt mixer or extruder without any solvent being incorporated in the process. In contrast, it is more efficient and low cost for industrial production than solution mixing [44]. High shear mixing at eminent temperatures attains the homogeneous mixing of graphitic materials and polymers. This method has comprehensively functional for production of thermoplastic composites [35]. However, this method showed thermal instability while dissolving the graphene fillers in thepolymer matrix [4, 36].

2.1.1.2 Mixed non-covalent and covalent dispersion

In situ polymerisation (Figure 4) involves the mixing of filler with a monomer or multiple monomers accompanied with polymerisation with the existence of dispersed filler. Later to have sample testing specimens leads to extraction or solution casting or precipitation. The technique is often used to prepare the nanoclay, cellulose, graphene polymer nanocomposites with polymers like polyethylene, PMMA, polypyrrole[37–40]. The main point of this technique depends on theadequate dispersion of fillers in matrix followed by in situ

polymerisation commenced either by heat or by the inclusion of an appropriate compound. During in situ polymerisation, the intercalation of graphene was increased the interlayer spatial distance and exfoliates graphene platelets. Thus produced a well dispersed graphene sheet throughout the polymer matrix after polymerization. Additionally, unlike solution mixing it does not require separate exfoliation process[41]. Therefore, this method produces free radical polymerisation with improved dispersion of the filler in the matrix that results in increasing the space [42–45]. Graphene nanoparticles can achieve the maximum level of dispersion without any restacking the layers by using in situ polymerization. The layers of graphene and its subsidiaries have been separated by polymerisation with prior intercalated with monomers. It often termed as interaction polymerisation, which has been appliedto graphene nanoparticles and graphene oxide derived polymer composites [46].

Additionally, in situ polymerisation method allows the covalent bonding among the functionalised sheets and polymer matrix through differentchemicalreactions. For instance, emulsion polymerisation able to done in aqueous solutions of graphene platelets [47]. Wei et al. showed areduction of graphene oxide with hydrazine in aqueous solution. The extraction of hydrophobic reduced graphene oxide was efficiently achieved that also containing thepolymer.

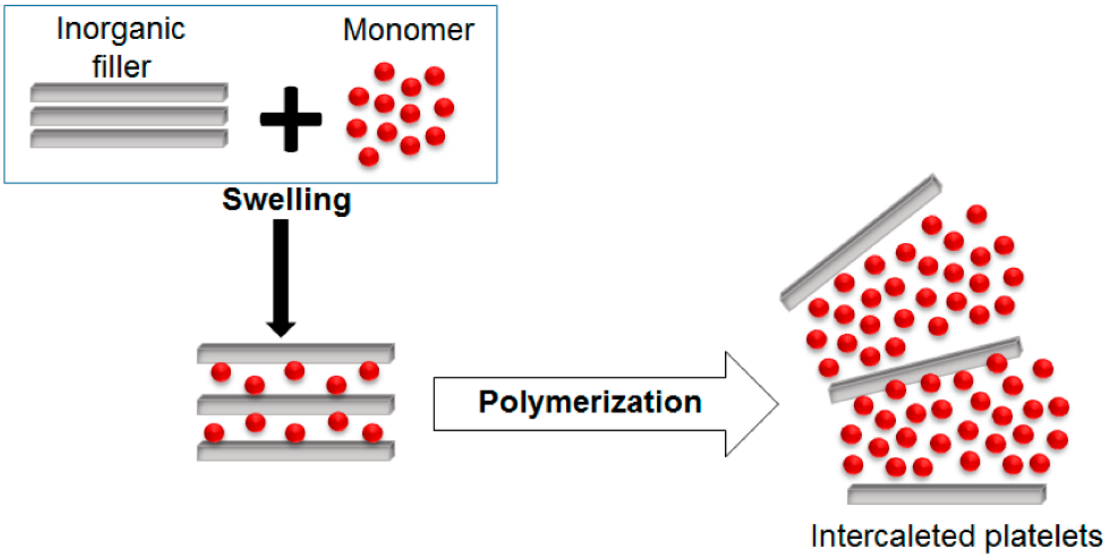


Figure 4 Schematic representation of the intercalation of monomers in-situ polymerisation[34].

While the larger interlayer spacing of rGO depending on relative humidity was between 0.6 and 0.8 nm when compared to graphite approximately 0.34 nm those provided the intercalation by both monomers and polymers[48]. There was an increase the layer spacing up to 2.2 nm when was intercalation of graphene oxide with polyvinyl alcohol [27]. Though, the significant disadvantage of this method was the viscosity rise with the evolution of polymerisation which obstructs the operation and minimises the load fraction [19].

2.1.1.3 Covalent dispersion

This section explains the covalent functionalization of nanoparticles framework. The variations of structures can take place either at the edges of the layers or on the surface. Surface functionalization is accompanied with alteration of one or more sp^2 carbon atoms into the sp^3 format of the carbon network by concurrent loss of the electrons [15, 21]. The covalent modification of graphene or other nanoparticles can be achieved through four different methods: nucleophilic substitution, condensation, addition and electrophilic addition [49–54]. The studies have shown that conducting polymers those composed of the heterogeneous blending of polymer functionalized graphene those

encapsulated with poly(3-hexylthiophene) and triphenylamine based poly(azomethine) [55]. The grafting to approaches with polystyrene (PS) chains, polyvinyl alcohol results in activation of polymer chains on the surface of GO[56–59]. Schematic illustration of surface functionalization was shown in Figure 5.

2.1.1.3.1 Nucleophilic substitution reaction

The nucleophilic reaction occurs in aqueous medium every easily at room temperatures. Thus, it results in favourable technique for significant production of functionalized graphene. The major responsive sites in the nucleophilic substation reaction are the epoxy groups of graphene oxide. The epoxy groups are attacked by the lone pair of electrons in the amine (-NH_2) functionality of the organic modifier [60]. Bourlions et al. reported the surface treated of graphene oxide through utilised various amines, $C_nH_{2n+1}NH_2$ (n=2, 4, 8, 12, 18) and amino acids [61]. For the small chain amines, the reaction completely took at room temperatures, while for long-chain aliphatic amines the mixture heated under vigorous stirring for 24 h.

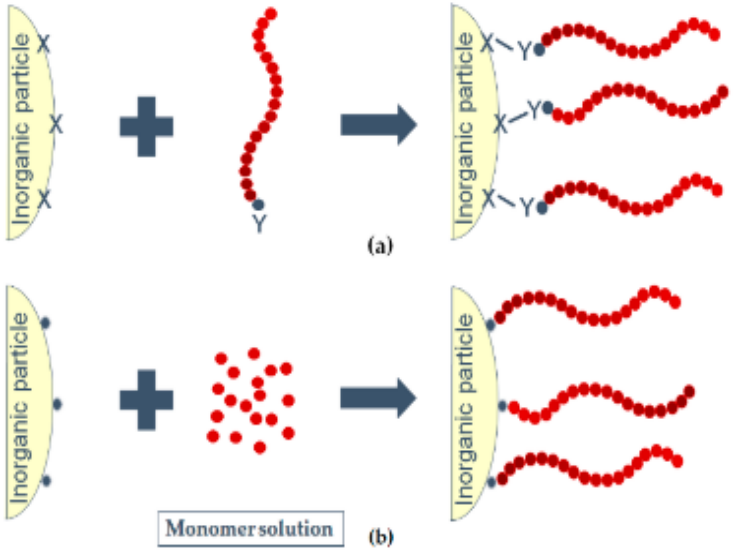


Figure 5 Schematic representation the surface functionalization of inorganic particles by (a) “grafting onto” and (b) “grafting from” reactions [34].

Pham et al. described a new process of modification by using a base material such as potassium methoxide with GO as a nucleophile. The prepared hybrid materials had a constant dispersion in water over three months and arose as a significant material accomplished of various requirements for potential applications [62]. For all type of aromatic amines, amino acids, amine terminated biomolecules, ionic liquids, small molecular weight polymers and silane compounds have been efficiently utilised in preparation of functionalised graphene [68], [69].

2.1.1.3.2 Electrophilic substitution

Electrophilic substitution reaction involves an electrophile to the displacement of a hydrogen atom [60]. Lomeda et al. and Zhu et al. synthesised organsoluable graphene through electrophilic substitution of aryl diazonium salt on the surface of surfactant-wrapped graphene sheets[63, 64]. The surface of reduced graphene oxide at pH ~ 10 was wrapped by surfactant sodium dodecylbenzene sulfonate (SDBS) later with hydrazine monohydrate. After that, the reduction process takes place at 80 °C for 24h, and the reduced graphene oxide was highly dissolvable in N, N-dimethyl-formamide (DMF) solvent. While these chemically functionalize graphene sheets are more dispersible in the solvents than the pristine graphene [65, 66].

2.1.1.3.3 Condensation reaction

A chemical reaction that involves two molecules those are functional groups combine to produce one single molecule with loss of entropy is condensation [60]. Stankovich et al. reported a series of isocyanate compounds for the surface alterations of graphene oxide through dispersing in DMF under nitrogen atmosphere which is useful when the preparation of polymer nanocomposites [67]. Shen et al. have prepared GObiocomposites with cysteine, adenine, ovalbuminand propyl amine with a two-step method at room temperature in buffer

solution. The functionalization of biocomposites acquired in short time [68]. Sulfanilic acid was used to surface modification of graphene oxide to study the electrochemical behaviour in the detection of hydrogen peroxide was done by Chen et al. as an ion-exchange material[69].

2.1.1.2.4 Addition reaction

Addition reaction involves two or more molecules in organic addition reaction that combine to create a large molecule. The most commonly used direct functionalisation organic species are dienophiles, free radicals and various reactive intermediates[60]. Vadukumpully et al. described the utilisation of various alkylasides for the wrapped graphene sheets surface modifications. The dispersibility of the functionalized graphene layers has been increased in organic solvents like acetone and toluene due to the presence of longer alkyl chains and polar functions groups on the surface [70]. Zhong et al. developed a simple and efficient approach for the synthesis of chemically converted graphene sheets through cycloaddition under mild reaction conditions[71]. The strategy of functionalisation of graphene sheets results in easily dispersion in water, toluene, chloroform and DMF. The functionalisation also helps in improvement of the conductivity of graphene at room temperature [72, 73].

Few polymers do not require any prior functionalization or grafting process to crosslink with graphene. The bonding can be formed during polymerisation. However, in the epoxy material a hardener like amine results in direct crosslinking also reacting with the prepolymer or isocyanate groups results in chain extender in polyurethane groups [74–76].

2.2 Graphene

Graphene was exfoliated efficiently a decade ago [77]. The innovation of free-standing graphene done by Andre Geim and Konstantin Novoselov at the University of Manchester in 2004 headed to the

award of the Nobel Prize in Physics 2010 “for ground breaking experiments regarding the two-dimensional material graphene” [78, 79]. Subsequently, there has been incredible attention from academia and industries in theinvestigation of graphene properties, production methods and potential applications [80].Graphene is a two-dimensional (2-D) single layer of sp^2 carbon atoms organised in a honeycomb network, and it possesses exceptional superior mechanical strength [81], electronic conductivity [82]and high thermal conductivity[83].

Graphene derivatives are pristine graphene, polycrystalline graphene, graphene oxide, graphene quantum dots and reduced graphene oxide. Pristine graphene is a single grain crystalline with faultless sp^2 bonded carbon atoms honeycomb lattice. The polycrystalline graphene is a single crystalline graphene grain arranged in different orientations through grain boundaries and it leads to dislocations defects. Grapheneoxide (GO) is a lattice sp^2 bonded carbon atoms. Reduced graphene oxide (rGO) formulated through chemical or physical reduction process with a precursor of graphene oxide and it shows the C/O ratio is higher than the initial GO. The nanoscale crystals of graphene that are small enough to yield excitation confinement and quantum size effect and its results showphotoluminescent properties that can be tailored depending on the size and surface chemistry [84–86].

Graphene and its derivatives have been broadly used as fillers in composites because of their outstanding properties. The properties of polymer-graphene composites depend on filler dispersion, theratio of filler to matrix and bonding between filler and matrix. The production methods and processes can alter these features. The benefits of graphene compared with other fillers is that it permits for enormous changes in the properties of composites at minimum percolation thresholds due to the ultrahigh aspect ratio of graphene. Though, the main disadvantage of using pristine graphene as a nanofilleristhe

strong van der Waals interactions between graphene sheets, resulting in reduced compatibility with most of the polymers. Hence the functionalization and stabilisation of graphene via modification are necessary to avoid the undesired aggregation and to maximise properties for the intended end-useapplication.

2.2.1 Fabrication of Graphene

One of the major concern of graphene since it was discovered has been discovering a production method that can only synthesis high quality graphene but also at board-scale. Synthesis of graphene was done by various methods such as mechanical exfoliation, chemical vapour decomposition, solvothermal synthesis, organic synthesis, graphene from graphene oxide via oxidation of graphite and extractionfromdifferent metal substrates [87–89]. The different graphitic forms are shown in Figure 7.

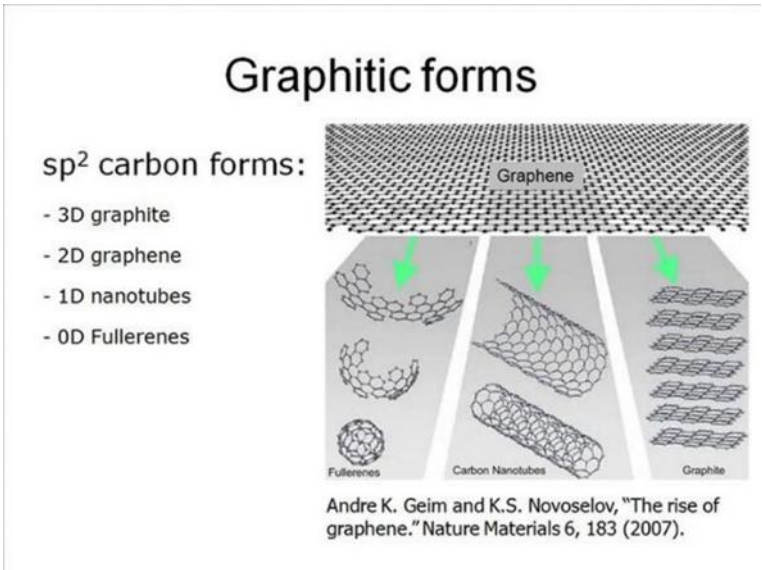


Figure 6 Graphitic Forms[85].

2.2.1.1 Micromechanical Cleavage

Micromechanical exfoliation is one of the graphene production methods, which is also known as scotch tape method that was extensively used in the field of crystallography. Among the other

processes in the research community, it is the most popular method for production of graphene and not astonishing this lead to 'birth of graphene' [77]. It is a simple method of peeling and replacing the adhesive tape. The technique involves in placing the graphene flakes in between the tapes and peel it until it achieves thin flakes with single layers. It did not require any specialised equipment whereas it simple and carried the synthesis easily.

Geimet al. used this method with repeated peeling of graphite in a sequence to achieve the substrate. Later dissolved the substrate in the acetone and Si wafer dipped into acetone solution where the flakes were attached to the surface of the waferdue to adherence force between oxidiser and graphene. This deposition may be due to van der walls for capillary forces. The layer sizes are up to 10 μm with single layers, and those are tested to study the electrical properties of graphene [78, 90]

However, it is an adaptable method but the main drawback is the capacity of production and it is still challenging to achieve. Despite challenges, the exfoliation is still the well-liked choice for fundamental research due to high-quality graphene production. It is accessiblefrom the perspective that it does not only start the revolution of graphene but also the large part of new devices and prototypes have been used this mechanically exfoliated graphene flakes. This technique still exists as the primary tool to study more about graphene properties and potential applications.

2.2.1.2 Liquid-phase exfoliation

The criticalprinciple of liquid-phase exfoliation (LPE) is to exfoliate graphite through dispersion of graphite in a suitable solvent and then ultra-sonicate or shear force to take out single or few-layer graphene sheets as shown in Figure 8. Graphite iscomposed by the weak van der Waals. In this method, the first step is to overcome the forces by effectively exfoliate the graphite. Wang et al.reported the value of

graphene surface energy to be 46.7 mNm^{-1}, while to decrease the surface tension between graphene layers and solvent there must be an appropriate portion of liquid that hasto resemble surface energy to exfoliate. Therefore, the solventssuch as N-Methyl-2-pyrrolidone (NMP), N-N-Dimethylformamide (DMF) havebeen successfully used to exfoliate and stabilise graphene [91–98].

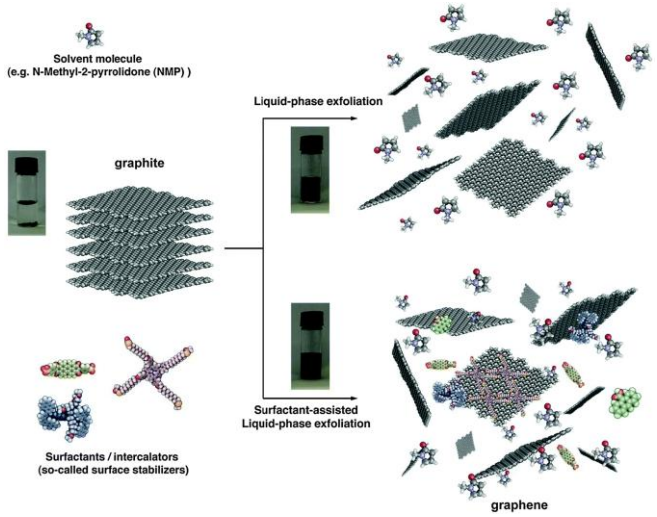


Figure 7 Schematic representation of the liquid-phase exfoliation process of graphite in the absence (top-right) and presence (bottom-right) of surfactant molecules of graphite[99].

Wang et al. obtained a concentration of 0.95 mg cm^{-3} of 1-5 layers of graphene sheets by exfoliating graphite in the solvent of 1-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl)-indie[100],[101]. Zhang et al. stated that the dispersion at low concentration was very unstable but showed sedimentation after a week. Initially, in that process graphene was exfoliated in NMP followed by filtration and additionally re-dispersed into ethanol. Finally, it was washed and repeatedly centrifuged to obtain the stable graphene at low concentration [96]. Guardia et al. carried out another investigation through ionic and non-ionic surfactants to exfoliate graphene. Whereas, non-ionic surfactants arebetter than the ionic regarding stabilising. It is also significant tonote that utmost of the surfactant systems acts as an insulator, thus, using surfacants effects in cooperating or reducing the conductive properties of graphene [102]. It was also stated that Pluronic-123 display excellent results through

sonication of 2 to 4 h [103]. Bari et al. described a high concentration of graphene 5.8 mg cm^{-3}, through dispersion of graphite in 1, 3- Bis (phenylmethyl) imidazoliumbis(trifluoromethyl-sulfonyl) amide for 1 h in bath sonication [104]. Nuvoil et al. attained graphene of 2 nm by having a low yield through sonicating in 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIM) for 24 h [107].

The major challenge in the graphene production through liquid-phase exfoliation is that the size of graphene flakes very toughto be controlled. It is acost-effectivemethod and malleable process for exfoliation of graphite to graphene.

2.2.1.3 Reduction of graphene oxide

Production of graphene via graphene oxide is a popular method due to high capacity in size and shape changing, inexpensive and can scatter well with functional groups of solvents. The process of preparation of graphene oxide from graphite popularly known as Hummer's Method [105]. It involves the intercalation of graphene with functional oxygen groups on the surface of graphene sheets. These functionalised graphene sheets were dispersed and stabilised in water easily with help of functional groups on surface of graphene sheets [106]. Dimiev et al. stated three main steps those required in converting graphite to graphene. Initially, graphite intercalated with sulphuric acid, later oxidised to produce GO and lastly dispersed in water[107]. The Hummer's method involved in highly toxic and explosive process at high temperatures with flammable materials like sodium nitrate, potassium permanganate and concentrated sulphuric acid. Potassium permanganate reacts with sulphuric acid from an oxidising agent that release toxic gas of dimanganese epoxide (Mn_2O_2) where this viscous reaction destroys the sp^2 structure and introduces functional groups of hydroxyls and carboxylic in basal or edge planes. Ithelps graphene oxide to dispersein water. Sodium nitrate releases toxic nitrous gas that makes the method unsuitable for large-scale fabrication. To

overcome this modified Hummer's method is introduced through eliminating sodium nitrate [86]. However, the oxidation commences few defects in graphene sheets and those defectscan be partly reduced through reduction process. Although graphene or rGO can be obtained from graphene oxide through reduction process none of these methods canfully restrain the transparent graphene sheets without defects after oxidation [84].

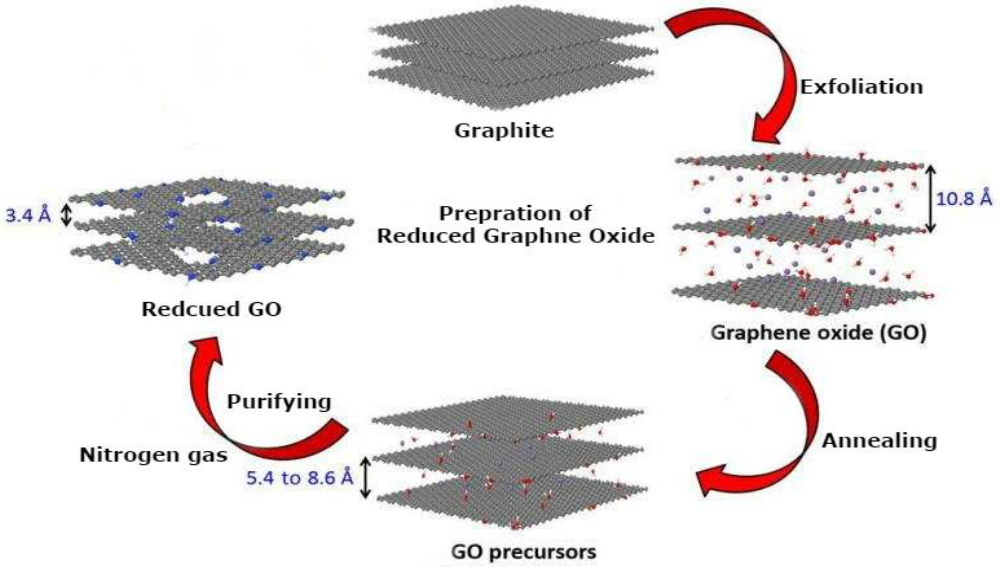


Figure 8 Reduction of rGO from graphite [105].

Table 1 Reduction agents of GO [108].

Reduction agents	**Temperature and time (C&h)**	**C/O ratio**	**Conductivity, σ (Sm^{-1})**
Hydrazine hydrate	100 °C; 24 h	10.3	2420
Thermal, Hydrogen gas	700 °C; 3 min	28.6	8100
$NaBH_4$	80 °C; 1 h	4.8	82
NH_3BH_3	80 °C; 12 h	14.2	19300
DMF+0.6M H_2SO_4	RT;1 h	8.4	1223

Zn/HCL	RT; 1 min	33.5	15000
Zn filings/ H_2SO_4	RT; 2 h	21.2	3416
Zn(powder)/NaOH	RT; 20 min	17.96	7540
Zn(powder)/NaOH	RT; 1 min Ultra sonication	33	14200
Mg(ribbons)/HCl	RT; 5 min	10.12	---
Solvothermal Sodium + ethanol	220 °C; 72 h	6.4	0.05
HI Hydrohalic acids	100 °C;1 h	12	298
Yeast	35-40 °C; 72 h	5.9	43
Polyethylene imine	80 °C; 2 h	5.6	0.783
Vitamin C	95 °C	12.5	7700
Isopropanol	100 °C; 5 days	6.9	1019
Benzyl alcohol	100 °C; 5 days	30	4,600

*RT – Room temperature.

The reduction process by using reducing agents such as hydrazine hydrate, sodium borohydride, dopamine, ascorbic acidare listed in Table1[67, 109–114]. The process also includes annealing process, where the graphene oxide is purified and reduced in the inert gas, such as nitrogen, argon, carbon monoxide environment to obtain rGO with high C/O ratio[36, 88, 115, 116]. The reduction process to fabricate rGO (Figure 9) is very low cost method with an advantage in the large-scale production. Besides, there is still research carrying

furtherly to find user-friendly and minimum toxic chemicals with less wastage.

2.2.1.4 Mechanical milling and electrochemical exfoliation of graphite

Antisariet al.reported the production of graphene from graphite through milling technique [117]. They managed to fabricate few-layer graphene by distributing graphite in water for 60 h. Ball millingwas demonstrated by Zhao et al. in a different liquid media to scatter the graphite flakes and later to produce graphene[118]. However, the milling technique depends on parameters such as the speed of rotation, milling type, the diameter of the ball, type of graphene and the concentration of graphite in a solvent[118]. Sun et al. investigated the production of graphene sheets production through co-processing graphite with cellulose with and melamine [119][120].

Electromechanical exfoliation is a conventional technique that has been usedforthe past few decades and it is mostly found in metal industry. Concurrently, extensively carbon materials are used as electrodes in electrochemistry due to outstanding electrical properties. Because of their exceptional electrical properties, graphene and graphite have been used as electrodes in devices for example batteries, solar cells, capacitors [121]. In current years, researchers successfully executed a method with simple electromechanical technique to fabricate graphene from natural graphite [89, 122–124]. The electromechanical exfoliation method is different from Hummer's method that uses active chemicals. The electromechanical technique involves in reduction and oxidation processes at the cathode and anode in the presence of an aqueous or organic electrolyte [125]. The main advantage of this method was the possibility of mass production of graphene at a much lower cost. Table 2 showed the advantages and disadvantages of various methods for producing graphene.

2.2.2 Properties of Graphene

The marvellous research in graphene is due to its exclusive properties and that declared material with a high possibility for various applications in industries and devices. Notably, outstanding properties have been reported with single layer flaws free graphene and this section briefly discussed few excellent properties.

Table 2The limitations in graphene production methods [79]

Method	Advantages	Disadvantages
Micromechanical Cleavage	• High-quality flakes • Simple preparation method • Low cost and easy • No special equipment needed	• Low yield • Uneven films • Dimensions dependent on initial crystal size
Graphene via Graphene Oxide	• High dispersibility • Scalable Method • High Processability • High Yield • Relatively inexpensive	• Poor electrical properties • Fragile stability of the colloidal dispersion • Potentially explosive process • Time-consuming • Use of toxic chemical • Small area flakes • Reduction to graphene is only partial
Liquid-Phase exfoliation	• High quality • Good scalability • Low temperature • Relatively inexpensive	• Small area graphene flakes (<5 μm) • Low yield of thin graphene layers • Limited dispersibility • Limited processability
Electrochemical	• High yield	• Inhomogeneous

Exfoliation	• Cost-effectiveness • High processability • Environment-friendly • Scalable • Fast production	flake thickness • Slight oxidation • Low yield
Mechanical Milling of Graphite	• Simple technique • Control over the various process parameter • Relatively inexpensive	• Long processing time • Induces defects • Low graphene concentration

2.2.2.1 Electronic Properties

The revolution of graphene initiated with electronic and electrical properties studies. K. S. Novoselov et al. reported the perspective of single-layer graphene in transistors applications with potential charge carries from holes to electrons [77]. However, if the layers of graphene are increased it would become weaker due to electrical field screening by other layers, also there is quantum Hall effect because of considerable electron mobility at different temperature and exposure to magnetic fields [126]. The quantum Hall effect of graphene for both electrons and holes has been found 4 e2 h-1 where e is electron charge and h is Planck's constant[126]. Due to the graphene band structure, the effect only happens at half number [127]. Additionally, the flexibility of electrons depends on the temperature and substrate. Bolotin et al. revealed that the alternating mobility greater than 200,000 $cm^2 V^{-1} S^{-1}$ with graphene dissolved and annealed on Si/SiO_2 ; this can be used as a semiconductor material [81].

2.2.2.2 Mechanical properties

Graphene shows utmost mechanical properties due to carbon-based materials. The carbon family have naturally displayed magnificent

mechanical properties, for instance, consider diamond a hardest natural material and CNTs with high tensile strength[128]. Lee et al. reportedgraphene to be thehardest material known by nanoindentation using an AFM, with a tensile strength of 130 GPa[129]. Similarly Frank et al. calculated the Young's modulus of single-layer graphene to be 0.5 TPa using AFM [130]. Through chemical cross-linking Dikin et al. synthesised graphene oxide paper that exhibits modulus around 32 GPa and tensile strength at 120 MPa[131].

2.2.2.3 Thermal properties

The intrinsic thermal conductivity of the graphene is approximately 2000-6000 $Wm^{-1}K^{-1}$at room temperature [82, 132–134]. Whereas the values are much relayed on the defects of graphene scattering edges, isotopic doping and residual fabrication [16, 130, 135]. Baladin et al. ulitised mechanical exfoliation technique to produce graphene sheets and measured the thermal properties. The thermal conductivity was in the range of 4800-5300 Wm^{-1} K^{-1}, which is higher than natural diamond ~2200 $Wm^{-1}K^{-1}$ [134, 136–138]. Caiet al.reported the thermal conductivity of graphene obtained through chemical vapour deposition (CVD) achieved up to 3000 Wm^{-1} K^{-1}[139] whichwashigher than that of copper. Notwithstanding with the thermal conductivity, the graphene has been used in different applications of manufacturing devices like heat dissipaters, sensors and flame retardants.

2.2.2.4 Chemical properties

Functionalization is required for graphene to make the surface reactive with other material because pure graphene is unreactive.The chemistry of graphene sheets is controlled through its surface, whereas graphene in the form of nanoribbons is controlled through its edges.Sharma et al. described that single-layer graphene is ten times high in reactivity when compared with multi-layer graphene. They

used disorder (D) peak in Raman spectroscopy to evaluate the layers. Furthermore, to identify the same property they also matched reactive edges of graphene with other materials using spectroscopic test and found that edges weremore reactive in bulk single graphene sheets [140]. Nitrene was used to activate the graphene sheets chemically. It means covalently linking the graphene surface with hydroxyl, carboxyl, bromine, and amino [73]. The process was to produce functionalised graphene sheets that can be used to prepare polymer composites and nanohybrids with high dispersion.

2.3 Boron Nitride Nanotubes

Boron nitride nanotubes (BNNTs) are known as "white graphene" and structural analogues of carbon nanotubes (CNTs) with better properties[141–143]. Even though they have structural resemblances, they considerably vary in their physical and chemical properties. BNNTs have alarge band gap of about 5.5 eV with exceptional radiation shielding properties when compared to CNTs[144]. Subsequently, the BNNTs are developed of B and N atoms;their electronic structures are predictable to be reasonably contradictory to that of CNTs. Some significant properties of BNNTs are high hydrogen storage capacity, high hydrophobicity, radiation absorption and resistance to oxidation[145, 146]. Because of their highly hydrophobic character, BNNTs are also used to produce super-hydrophobic surfaces [147, 148]. The source of this super-hydrophobicityiss featured to the surface morphology and adsorption capacity of BNNTs for airborne molecules [148]. BNNTs can be used in potential applications such as electronic devices, molecular biology and polymer composites[149].

Bansal et al. synthesised glass composite by addition 4wt % BNNTs and measuredthe strength and fracture toughness as 90% and 35%, which were better than that of CNTs [148, 150]. Additionally, medical and biomedical applications of BNNTs has been increasingly investigated [151–155].

2.3.1 Synthesis of BNNTs

The synthesis of BNNTs was initially documented by Chopra in 1995 through arc discharge method. It was followed by various methods like chemical vapour discharge method, ball milling reactions, laser ablation and low-temperature methods [154, 156–173].

BNNTs synthesised through arc discharge method showa length of 200 nm and the inner diameter of 1-3 nm. An arc discharge isproducedwithhexagonal BN filled tungsten rod acts as an anode and a cooled copper electrode acts as a cathode. The BNNTs in dark grey colour aree gatheredfrom the surface of the copper cathode. Similarly, BNNTs areeacquired from using hafnium diboride (HfB_2) electrodes and conductive boron substance such as YB_6[160, 161, 163].

BNNTs can also be produced from CNTs by substitution reactions. The synthesis isscarried out with CNTs, B_2O_3 under nitrogen gas atmosphere at 1773 K. The same reaction iscarried out under ammonia gas at 1260 °C for 30 min to obtain high yield BNNTs [159, 174, 175]. The reaction under inert gas atmosphere is given below

$$B_2O_3 + 3C(CNTs) + N_2 \rightarrow 2BN(BNNTs) + 3CO$$

Chemical vapour deposition (CVD) is a familiar method that is a low-cost method and most commonly used for any material synthesis. Therefore, it produces high strength products with a simple procedure. The synthesis of BNNTs using borazine ($B_3N_3H_6$) was reported by Lourieet al.[176]. Theproduction of high quality of BNNTswas achieved with the help ofcatalysts like Co, Ni, NiB and Ni_2B. Furthermore, NiB and Ni_2B were used as precursors to achieve highest quantity BNNTs [177–183]. CVD process with different type of reactions are stated below

$$2MgO_{(s)} + 2B_{(s)} \rightarrow B_2O_{2(g)} + 2Mg_{(g)}$$

$$2FeO_{(s)} + 2B_{(s)} \rightarrow B_2O_{2(g)} + 2Fe_{(g)}$$

$$B_2O_{2(g)} + 2NH_3 \rightarrow 2BN_{(s)} + 2H_2O_{(g)} + H_{2(g)}$$

Ball milling is another technique that mostly used to increase the surface area and to help in bringing the catalyst contact with boron and nitrogen at asubstantialamount of possibility. Li et al. demonstrated the ball milling synthesis by using amorphous boron powder, ferric nanohydrate and obtained high yield BNNTs [184–187]. While in another study,it was reported that the production of BNNTs was achieved with ball milling at 155 rpm for 150 h with only amorphous boron under ammonia atmosphere [188].

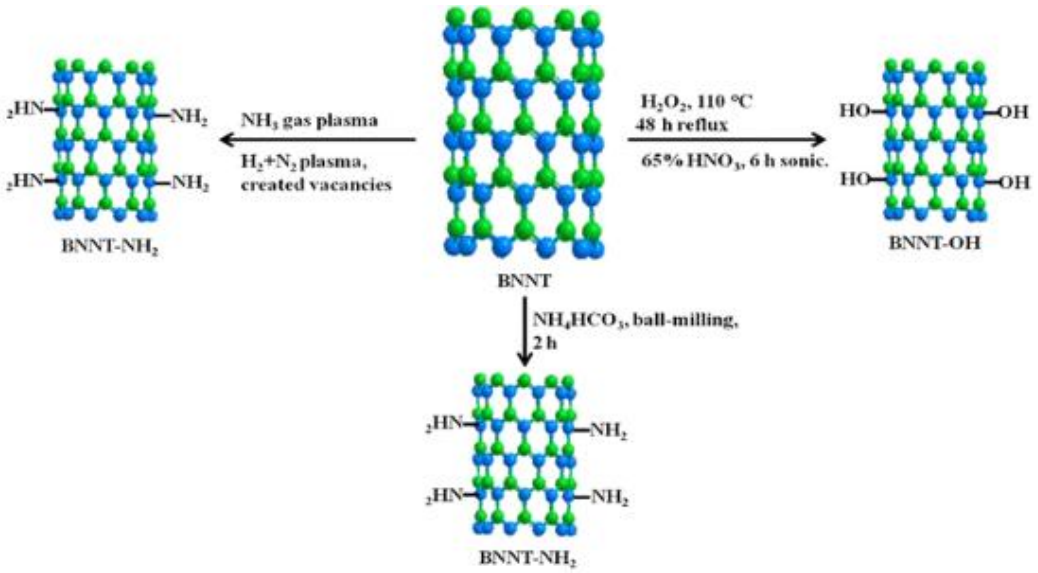


Figure 9 Summary of chemical modification routes of BNNTs [189].

2.3.2 Boron Nitride Nanotubes properties

BNNTs are stable in air up to 800 °C chemically and thermally. They offer super thermal conductivity with excellent young's modulus, i.e., ~1.8±0.3 TPa and shear modulus at 7±1 GPa as well as exhibit superhydrophobicity[147, 167, 190–194]. BNNTs show notable feature about the band gaps, that they are tuneable by doping with carbon [195], radial deformation [196] or by applying a transverse electric field across the BNNTs [197]. The electrical transport properties of BNNTs canbe efficiently modified from insulating to semiconducting by a bending deformation[194]. Bai et al. described that under in situ elastic bending deformation at room temperature inside a 300 kV high-

resolution transmission electron microscope, a typical electrically insulating BNNTs may convert to a semiconductor [153, 198–201].

The various types of precursors and methods for synthesising different shapes of BNNTs and the physical properties of the products were tabulated in Table 3.

Table 3 BNNTs synthesis methods and properties [173]

Precursor	**Temperature (°C); Time (h)**	**Method**	**Growth Mechanism**	**Physical Properties**
B, h-Bn, NH_3	<1100; 2	Ball milling (20 h), CVD	Base	40-100 nm dia., bamboo or cylindrical shape
B:FeO;MgO (2:1:1), NH_3	1200; 0.5	Mechanic Mixed CVD	Base	30nm dia., random direction closed tip ends
	1300; 0.5		Tip	60 nm dia., random direction closed tip ends
	1400; 0.5		Mixed	10 nm dia., flower-like closed tip ends
B:FeO:MgO (1:1:1) NH_3	1300; 0.5		Tip / base	100-500 nm dia., closed tip ends

B:FeO:MgO (4:1:1) NH_3	1300; 0.5		Tip / base	50- 150 nm dia., closed tip ends
B_2O_3, CaB_6, Mg, NH_3	1150; 6	CVD	base	150 nm dia., >10 μm length
h-BN, N_2	1250-1300; 10	Ball milling (100h), CVD		30-60 nm dia., cylindrical shape 500nm length
B, FeO, MgO	1100-1700; 1	Ball Milling, CVD	Metal catalytic	50-80 nm dia., up to 10 μm length straight nanowires
B, Iron particle, N_2	1100; 15	Ball Milling (50h), CVD	Metal Catalytic growth	50-200 nm dia., up to 1mm length bamboo-like
MWCNT, H_3BO_3, NH_3	1300; 3	Substitution		40-50 nm dia.,
B,$CO(NO_3)_2$,N_2, H_2	1100; 0.5-3	Ball milling, CVD		Bamboo like

B, N_2	1200; 16	Ball milling (150h), CVD		20-50 nm dia., cylindrical or cylindrical capped by iron bamboo like
KBH_4, NH_4Cl, N_2	1200-1300; 5-10	CVD		10-30 nm dia., up to 5μm length bamboo-like structure
V, Fe_2O_3, NH_3	1200-1300; 2.25	CVD		64-136 nm dia., bamboo-like structure
MWCNT, H_3BO_3, NH_3	1080; 6	Substitution		10-100 nm dia., 10μm length
Ammon. borane, Ferrocn., N_2	1450; 1	CVD	(Large dia., catalyst) or Vapour-liquid-solid (small diam. Catalyst	300nm dia., 10μm length bamboo like or 15-200nm dia., 10μm length cylindrical shape
B, Fe_2O_3, NH_3, B,Fe^{3+}-MCM-41, NH_3	600; 1	CVD		20-60 nm dia., 2.5-4 nm dia.,

YB_6, N_2/Ar		Arc discharge	Mixed growth	4-10 nm dia., 4-6μm length, Closed or open tip

2.4 Graphene polymer nanocomposites

Graphene has been introducedinto epoxy based materials to improve different functional properties. Bortz et al. examined the influence of graphene concentration on the mechanical properties of graphene/epoxy nanocomposites. The tensile strength of unmodified epoxy improved by approximately 12 % at only 0.1 wt% graphene oxide loading [202]. Wajid et al. used solution mixing to produce graphene/epoxy composites. The elastic modulus and tensile strength enhanced by 38% and 37% respectively at only 0.46 vol% loading of graphene[203]. Nguyen et al. utilised reduced graphene oxide sheets (rGO) and amine-modified nanofibrillated cellulose (A-NFC) to prepare composites with improved properties[204]. These composites showed better electrical conductivity of up to 71.8 S m^{-1} and tensile strength of up to 273 MPa. Graphene-cellulose paper (GCP) membranes are employed to produce flexible supercapacitors [205]. Wang et al. fabricated a PANI/graphene composite paper (GPCP) by in-situanodicelectropolymerization (AEP)[206]. This graphene/polyaniline composite exhibited a stable large electrochemical gravimetric and volumetric capacitance of 233 F g^{-1} and of 135 F cm^{-3} also shown a tensile strength of 12.6 MPa. Liang et al. studied the dispersion of graphene with poly(vinyl alcohol) (PVA) [25]. In this study, water was used as the solvent to disperse graphene into the PVA matrix. The tensile strength increased by 76% and elastic modulus by 62% at graphene loading of 0.7 wt%. Kim et al. investigated polycarbonate (PC) composites doped with graphite and functionalized graphene sheets (FGS) by the melt intercalation method. Both graphite and FGS

fillers enhanced the strength and stability PC composites[207]. Homogeneous dispersion reduces the creation of concentrated local stresses and promotes even load allocation throughout the matrix [208, 209]. However, attaining better dispersion is still a critical challenge, due to graphene has a strong interaction among the layers because of the van der Waals force and therefore leads to agglomerate irreversibly or even to restack into graphite-like structures in the polymer matrix [210]. Functionalization of the graphene surface can be made to imrpovethe interaction of graphene and the polymer matrix, but regulating other circumstances such as graphene orientation, graphene contact, i.e. plane-to-plane, edge-to-plane, edge-to-edge remains a huge problem.

2.5 BNNTs polymer nanocomposites

There are not many studies on BNNTs reinforced compositeshave been reported[146, 150, 211]. Researchers have incorporated BNNTs into glasses mainly to upsurge the strength and fracture toughness [146, 154, 201]. Another study on BNNTs-ceramic composite to improve the superplasticity in Al_2O_3 and Si_3N_4 with theaddition of BNNTs was reported [211]. Few studies by researchers have been reported polymer interface with BNNTs such as polystyrene, polyaniline, acopolymer of vinylidence chloride and acrylonitrile, and acopolymer of L-lactide and ε-caprolactone[151, 166, 188, 212–215]. BNNTs have higher chemical stability than CNTs in oxidative atmosphere, with their oxidation starting at 950 °C compared to CNTs at 500 °C. It has been reported that there was a noteworthy enhancement in the mechanical properties of PLA, PCL and copolymer PLC with the addition of CNTs[216, 217]. However, the physical property investigations exposed that BNNTs' display stable wide band gap, superb mechanical strength, high thermal conductivity, and ultra-violet light emission those different from CNTs. Motivated by this scenario, BNNTs

incorporated with PCL polymer and to investigate the mechanical and thermal properties was proposed in this study.

2.6 Biocompatibility of polymer nanocomposites

Nanocomposites have led to fast growth in the biomedical applications. However, there is inadequate understanding of the environmental health and safety aspects of nanocomposites. It remains a significant barrier to thefuture growth of nanocomposites in medical applications. Therefore, it is essential to develop toxicity assays using intact animals.

2.6.1 *Caenorhabditiselegans* for biocompatibility testing

Forthcoming advanced materials for biological applications could consist of different types of resources that areable to respond precisely to the surrounding biological matters. Thus, it isrequired to predict the corresponding conditions of the reactivity in between the systems and materials, i.e., the degradation of the nanoparticles and the interaction with the organic environment. Whereas the chemical structure and properties of nanoparticles characterised and controlled, but the interface of living organisms and biological fluids with composites has not been in-depth evaluated. Commonly, the evaluation of materials for biological application is done at the last stage, which results in suspending the optimisation of materials. Additionally, testing will be done through in vitro process with animals involving high cost and order of animals. Thus, an assessment that helps in providing useful biological data at low cost is in enormous demand [218].

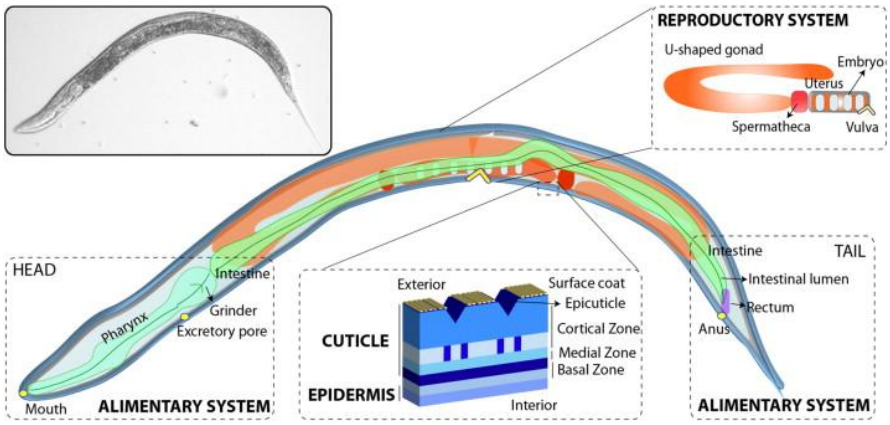


Figure 10*C. elegans* anatomy and the parts of interest for nanoparticles[219]

Caenorhabditiselegans (C. elegans) is a living nematode with 1-mm long that claimed as an animal model by Sydney Brenner in 1965 [220]. *C. elegans*are the first multicellular organisms with mostly hermaphroditic; theyhavegeneses and biochemical paths like humans. The structure of the *C. elegans* built up with the alimentary tube, the cuticle and epidermis shown in Figure 5. There is another tube in the alimentary tube the space between two filled with a fluid called the pseudocoelom. The microorganism consists of a reproductive system, nervous system, alimentary system, and an excretory system those shield by the cuticle. *C. elegans* also helps in reduction of time for cell-culture assays and eliminate the problems arose while using mammalian models. It can produce hundreds of single laboratory dish with short lifespan approximately 2 to 3 weeks also it was advantageous with fast life cycle with 3days [220]. Through this genome size model nanomaterials can be evaluated the effects on reproduction, toxicity mechanisms, and effects on exposed worms (skin, oral). The nanomaterials are introduced to model through feeding (cuticle), the excretory pore and injection to the specified part of *the C.elegan*.[219].

Levardet al. studied the effect of pristine silver nanoparticles through feeding process and identify the effects occurred in ion- and particle specified [221]. The morality and impacts on the growth of *C.*

*elegans*were described when it was exposed to sulfurised silver particles. Additionally, it was compared with silver nanoparticles AgNPs[222] Daniel L.Starnes et al. described the bioavailability of silver nanoparticles in wastewater treatment process through using *C. elegans*to know the toxicity levels of Ag when decomposed into soil such as pesticides [223]. There are few other nanoparticles tested including metals such as TiO_2, Al_2O_3 and ZnO_2 [224–227]and carbon nanotubes, graphene oxide [228–230]. Ning Wang et al.utilised boron nitride nanomaterials and evaluated the in vivo whole animal model. The study showed higher biocompatibility of pure BNNT and less toxicity through oxidative nature of boron nitride [231].

Furthermore, statistical and analytical analysis of the material characterised by various methods like SEM for the mechanical properties of the material. Whereas, the biomedical characterisation of the material carried out with a *C.elegans* animal model to test the toxicity and biocompatibility of the nanocomposite.

2.7 Applications of polymer nanocomposites

The enhancements in mechanical properties of nanocomposites have arisen a significant interest in many automotive and general/industrial applications. It includes possible for use as mirror housing on different types of vehicles, belt covers, engine covers, and door handles. More universal applications consist of packaging, solar cell, plastic containers, fuel cell, impellers, fuel tank, blades for vacuum cleaners, gas barriers, products for low flammability[10, 15, 232–235]. Figure 6 showed the schematic view of different applications of polymer nanocomposites.

2.7.1 Graphene polymer nanocomposite applications

Graphene-PANI nanocomposites have also been invented for hydrogen sensing applications [236]. Hydrogen sensing of the nanocomposite was matched with the pure PANI and graphene. Thus found

nanocomposite films have higher sensitivity than the pure films. Numerous current improvements contain the development of multicomponent polymer nanocomposites commencing from silica and other oxide particles coated with graphene oxide for recognition of dopamine [237] and observing of mammalian nerve cells, proteins and *Escherichia coli* cell [238, 239]. The rGO-polymer with theelectrochemical sensing of poisonous gas was introduced[240].

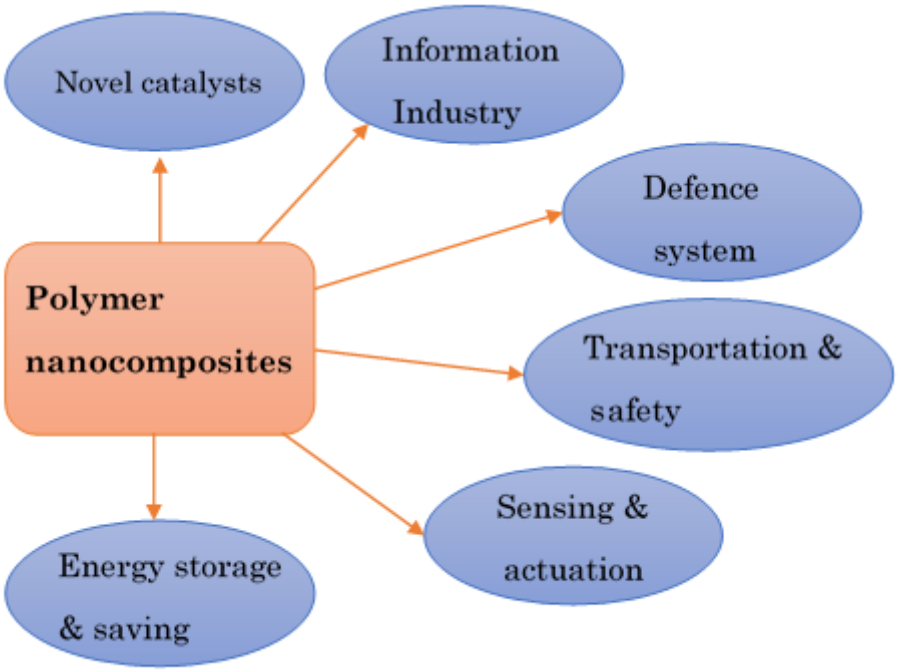


Figure 11 Polymer nanocomposites applications

In present research of materials, graphene was considered for the use of gas barrier and gas sensor application due to its non-permeable sheets-like structure. Yang et al. coated GO sheets with PET polymer to form a thick layer polymer nanocomposite to study the oxygen barrier properties [241]. Similarly, a high selectivity of hydrogen sensors fabricated by using graphene has been reported with copolymer nanocomposites [242, 243]. Graphene can be an essential photovoltaic material because it is able to act as a hole transport. Chhowalla et al. described the use of graphene oxide as substitute solution for hole-transport material in organic photovoltaic film

[244].Ahadian et al. produced hydrogel-graphene biomedical materials through preparing a stable aqueous graphene distribution in aqueous bovine serum albumin (BSA) solution[245]. Then, ab initio calculations were used to disclose the molecular interfaces between graphene and BSA. The outcome showed a mechanically stable and tunable hydrogel-graphene material, which is of excessive attention for cell-based research.

2.7.2 Boron nitride nanotubes polymer nanocomposites applications

One of the fascinating application of BNNTs was in the area of sensors. A sensitive humidity sensor was developed with BNNTs and silver nanoparticles for fast recognition of humidity. The adsorption-desorption assessments presented that the AgNP–BNNT material had a hypothetically rapid reply/retrieval time of 100/15 s for the finding of relative humidity at room temperature[246]. BNNTs were also studied for their hydrogen adsorption capacity. Molecular dynamics simulations specified that the adsorption performance of hydrogen molecules in single-walled BNNTs differs according to hydrogen incident energy. The theoretical research of the hydrogen storage capacity of BNNTs disclosed that the nature of the electronic structure of boron and nitrogen atoms, as well as the diameter and dimensions of the BNNT walls have an influence on their hydrogen adsorption capacity[247, 248]. While there are limited numbers of reports, the investigations showed that BNNTs are promising materials for hydrogen storage. It is essential to note that additional investigations addressing the factors such as gas pressure, temperature and purity of the BNNTs should be done. Biomedical applications of BNNTs were studied on neutron capture therapy [249]. Gadolinium-doped BNNTs were prepared to apply in clinical operations such as MRI contrast agent. Because of high magnetic moment property of gadolinium, Gd

doped BNNTs shows a significant agent to label the cell populations and the structures[250].

It is clear that there is a rising trend for the application of BNNTs polymer nanocomposites and graphene polymer nanocomposites in several fields from sensors to medicine. However, it is yet to achieve the production of large quantities with high purity of graphene and BNNTs. Apart from it, toxicity was a significant issue that needs to study to increase the use of these materials in biological systems.

Chapter 3

Methodology

3.1 Materials

Expandable graphite, 220-50N was supplied by Graftech Inc. (OH, USA). Amorphous boron powder (B), iron (III) monohydrate (Fe(NO3)3.9H2O), ethanol 95% grade AR and urea (CO(NH2)2) grade AR, potassium permanganate grade AR (KMnO4, 99%), sodium borohydride AR (NaBH4, >98%), hydrogen peroxide (H2O2, 28%) and sodium nitrate (NaNO3, 99%) were purchased from Friendemann Schmidt Chemical (Parkwood, Australia). Ammonia (NH3, 99.5%) gas cylinder was purchased from Infinity Gas Sdn Bhd (Puchong, Malaysia). Graphite fine powder extra pure was obtained from Synergy Scientific Sdn Bhd (Kuala Lumpur, Malaysia). Polylactic acid (PLA) with a degree of polymerisation of 1700 and degree of hydrolysis of 88% was supplied by LGC Scientific Sdn Bhd (Selangor, Malaysia). Polycaprolactone (PCL, average Mn 80,000) with a density of 1.145 g/mL was purchased from Sigma Aldrich. Industrial nitrogen (N2, 99%) gas was supplied from Linde gas Sdn Bhd (Selangor, Malaysia).

3.2 Stage 1: Synthesis of nanoparticles

3.2.1 Synthesisof graphene oxide by Hummer's method

Graphene oxide (GO) was prepared from graphite powder by using Hummer's method[105], which is one of the most efficient and low-cost methods. In this work, 3 g of expandable graphite powder and 3 g of $NaNO_3$wereadded to 70 ml of concentrated H_2SO_4 in a glass beaker. Later the mixture was stirred continuously using mechanical stirrer for 1 h and the temperature was kept below 10 °C using an ice bath. Then 9 g of $KMnO_4$ was added steadily by keeping the mixture temperature below 20 °C. The mixture was mechanically stirred using mechanical stirrer for 1 h to get a homogenous mixture. Subsequently, 100 ml of deionised water was added to the mixture followed by

mechanical stirring for another hour. The beaker was removed from the ice bath when the colour of the mixture turned brown. After that, the stirring was continued for another hour and the temperature was increased to 35 °C. Then 150 ml of deionised water was added to the mixture as soon as the colour of the mixture changed from brown to light brown. The temperature was then increased to 95 °C and stirred for 1 h. Lastly, 10 ml of H_2O_2 and 150 ml of deionised (DI) water was added to achieve a light yellow suspension as the residual $MnO_2$and $KMnO_4$ formed in the solution were reduced to colourless soluble salts. The synthesised GO was hydrophilic. The solution washed with 1M HCL and water for repeated times until the pH value of the solution reached 7. Later centrifuged at 5000 rpm for 30 min to remove unexfoliated graphite and other impurities. The solution was then filtered and dried. Finally, a brown coloured GO powder was obtained.

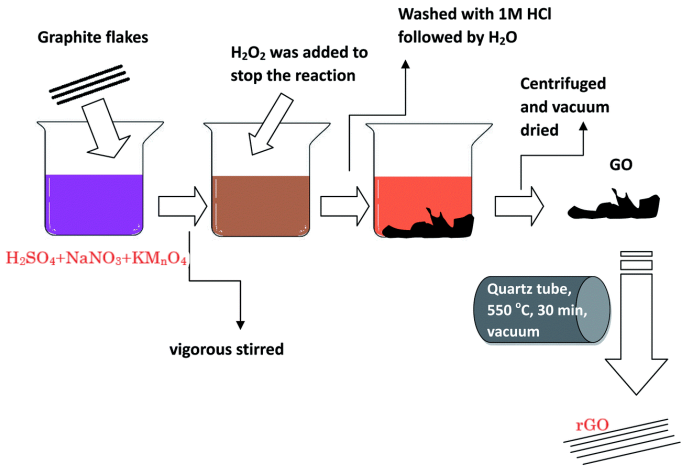


Figure 12 Schematic illustration of synthesis procedures of GO and r-GO [235].

3.2.2 Reduction of graphene oxide (GO)

The reduction of GO was carried out using reducing agent [109]. The solution was prepared by dispersing 5 g of GO in deionized water (1 mg ml^{-1}) followed by ultra-sonication to obtain a homogeneous dispersion. Later, 5 g of $NaBH_4$ was introduced into 50 ml of GO dispersion and the pH was adjusted to ~9-10. This solution was stirred continuously by using magnetic stirrer at 80 °C for 1 h. After vigorous stirring, the

dense precipitate obtained was reduced graphene oxide (rGO). Next, the rGO was filtered and repeatedly washed with deionised water until pH neutral. After that, the rGO was kept in a vacuum desiccator along phosphorus pentoxide for two days. Finally, the obtained rGO was loaded into an alumina crucible boat and kept in the tubular furnace at a temperature of 1000 °C in the inert atmosphere of nitrogen gas for 8 h and product acquired was graphene.

3.2.3 Synthesisof boron nitride nanotubes (BNNTs) through co-precipitation method

Primarily, iron (III) nitrate nano hydrate and urea were dissolved in DI water at room temperature and later amorphous boron (B) powder was addedto the solution at ratios of B: Fe^{3+}: $CO(NH_2)_2$ at 1:0.1:2 [251]. The slurry was kept in a water bath at the constant temperature of 80 °C and stirred for 5 h. After that, the slurry was taken out from the water bath and was preserved for a day to allow the reactions to occur. After ageing, the precipitated mixture was collected and washed with DI water and ethanol repeatedly to get rid of residual nitrate ions. The precipitate was dried in an oven at 100 °C for 5 h then an intermediate powder like $Fe(OH)_3$.B was formed. Subsequently, the dry intermediate powder was loaded into an alumina boat that was then placed at the centre of a tube and the tube was placed into a tubular furnace. Before proceeding to annealing process with the tubular furnace, the furnace chamber was flushed with high purity N_2 flow (1000 sscm) for 20 min to eliminate the residual air. The furnace was heated up to 800 °C in flowing N_2 (50 sscm) and kept constant at the same temperature for 1 h. After that, the furnace was heated continuously to 1200 °C and held for 3 h at thesame temperature in ammonia flow (50 sccm). Finally, the furnace was cooled naturally under N_2 flow at room temperature then the final precipitate obtained was boron nitride nanotubes (BNNTs).

Figure 13 Tubular furnace used for annealing process of BNNTs.

3.2.4 Synthesisof BNNTs-graphene hybrid

Firstly, to remove the humidity, the graphene and BNNTs powders were kept in a vacuum oven at 75 °C for 2 h. After that, the graphene and BNNTs were mixed with concentrated H_2SO_4 and HNO_3 at a ratio of 1:1 to achieve hybrid intercalated compound. The stable intercalation was obtained through stirring using mechanical stirrer for 12 h. Later, it was carefully filtered and washed with DI water for numerous times until pH neutral. Subsequently, the mixture was dried in vacuum oven for 12 h. After that, it was heated at 800 °C to obtain an expanded hybrid structure. Lastly, the mixture was undergone the final exfoliation through ultra-sonication in N, N-dimethylformamide (DMF) for 1 h to get graphene sheets incorporated with BNNTs. Then DMF was removed from the mixture through centrifuging at 5000 rpm for 8 h. Consequently, the BNNTs-graphene hybrid was collected for further characterisation.

3.3 Stage 2: Preparation of polymer nanocomposites

3.3.1 Preparation of PCL-BNNTs nanocomposites

To prepare the polymer nanocomposite, 1 g of PCL was dissolved with 10 ml of chloroform to form a colloidal solution by constant stirring using mechanical stirrer at room temperature[214]. A desired amount of BNNTs was mixed with 10 ml of chloroform and then combined with a PCL-chloroform solution[145]. The final mixture was ultrasonicated

for 30 min before casting in a 60 mm diameter glass petri dish. For pure PCL film, 1 g of PCL was dissolved with 10 ml chloroform solution and ultrasonicated before casting. This was done in order to keep the processing parameters similar for all of the composites. The composite films were vacuum dried for 24 h at room temperature. Consequently, they were peeled off from the glass surface and the thickness of free-standing films wasapproximately 0.5 mm for the composites. The composition prepared for this study were 100 wt% PCL, PCL- with 2wt% BNNTs, PCL with 5wt% BNNTs which will be referred as PCL, PCL-2BNNT, PCL-5BNNT respectively, hereafter.

3.3.2 Preparation of PLA-graphene nanocomposites

To prepare the PLA-graphene nanocomposite, 0.95 g PLA soaked in 10 ml chloroform overnight[252, 253]. The mixture was then subjected to magnetic stirring in the next following day to dissolve PLA entirely in the chloroform. In a separate beaker, a 0.5g of graphene was added to 10 ml of chloroform. The mixture of graphene with chloroform was ultrasonicated for 1 h and then mixed with the PLA solution. Afterthat, the PLA-graphene precipitate washed with excess methanol by using mechanical stirrer to reduce the residuals. After that, the mixturewas transferred to asiliconemold and dried at 50 °C for 12 h in an oven. Subsequently, the PLA-graphene nanocompositeswerehot pressed at 180 °C with 150 MPa for 5 min to obtain the film. The prepared samples of PLA-5 wt% graphene were refereed as PLA-graphene hereafter.

3.4 Characterisation

The nanohybrid and polymer nanocomposites prepared were characterised for their mechanical, thermal properties and biocompatibility. The mechanical and thermal analysis were carried out by tensile test and thermogravimetric analysis (TGA), respectively. The morphology test was performed by scanning electron microscope (SEM) and surface analysis by BET surface area analyser. The

absorption and density were investigated by UV-vis spectrometer and densitometer, respectively. The biocompatibility was performed using *Caenorhabditiselegans (C. elegans)*.

3.4.1 Morphology

The morphology of the polymer nanocomposites was studied by using FEI Quanta 400F Field Emission SEM. The PCL, PCL-2BNNT, PCL-5BNNT, PLA and PLA-graphene were broken into tiny pieces after immersing in the liquid nitrogen for 10 s. Through breaking into pieces cross-section of samples can be obtained from the fractured surface. The samples were mounted in vertical position with cross-sectional view on a mounting tape before scanning under accelerating voltage of 20 kV and high vacuum mode.

3.4.2 Mechanical Properties

The tensile and flexural properties were analysed through bench type tensile machine Lloyd Instruments LR50K plus. The tensile sample and tests were conducted in accordance with the ASTM- D3039M-08 procedure. The specimens were cut with dimensions of 120 mm (l) x 20 mm (w) at 2 mm (t), which were subjected to a persistent crosshead speed of 2 mm min^{-1}, and force-displacement was noted for nominal stress-strain behaviours. Each composition of the nanocomposites was tested and an average value of the respective property was calculated.

3.4.3 Thermal Properties

The thermogravimetric analysis of the samples were measured by usingPerkinElmer TGA-PT1000 instrument. 10-15 mg of the specimen was prepared and placed in an open alumina crucible. The samples were heated up to 800 °C from room temperature with a consistent ramping rate of 20 °Cmin^{-1} under N_2 condition at a flow rate of 50 ml min^{-1}.

3.4.4 UV-visible spectroscopy

A UV-vis spectrophotometer (UV 3500 Shimadzu, Japan) operating between 200 to 900 nm was used in order to record the spectrum of the BNNTs-graphene hybrid composite. The samples were tested in the liquid from where the hybrid nanocomposite was ultrasonicated in DMF to form a colloidal solution. Later the colloidal solution was kept in the sample holder of UV- visible spectrometer along with reference solution that is DMF clear solution. Subsequently, the results of absorbance were noted down by passing the UV light source.

3.4.5 Density measurement

The density of polymer nanocomposites PCL, PCL-2BNNTs, PCL-5BNNTs were measuredby using densitometer DMA™ 500. The colloidal solutions of nanocomposites of about 5 ml were loaded through the sample supply. The density of samples wasrecorded at 35 °C.

3.4.6 X-ray diffraction (XRD)

X-ray diffraction of BNNTs was carried out using Cu Kα (λ=1.542 Å) radiation in a Siemens D-500 X-ray diffractometer operating at 45 kV and 35 mA. 1 mg of the sample was placed under the X-ray to identify the peaks corresponding to different phases of boron nitrides.

3.4.7 BET surface area analysis

Brunauer-Emmett-Teller (BET) measurements were carried out to measure the porous characteristics of the prepared samples of BNNTs and BNNTs-graphene. The adsorption and desorption of isothermal of the products were identified as IUPAC type III, which is the feature of macroporous materials.

3.4.8 Biocompatibility tests

The biocompatibility tests were carried out on a Caenorhabditiselegans (C. elegans). Graphene and PLA-graphene materials were sterilized by autoclaving at 121°C for 21 minutes. A standard amount of 2 mg mL^{-1} graphene and PLA-graphene was prepared by adding 1 ml of DI water to 2 mg of materials. Both the materials were tested at 50, 200, 500 and 1000 µg mL^{-1}. The corresponding concentrations were added to *C. elegans* foods source. Escherichia coli (E. *coli*) OP50 and 50 µL of bacteria combined with nanocomposites were seeded onto the surface of Nematode Growth Medium (NGM) agar in a 3.5 cm Petri dishes (this plate was known as assay plate). E. *coli* OP50 was killed by heating the culture at 80 °C for 30 min. This was done to eliminate any possible effect of the nanoparticles on E. *coli* OP50 which may, in turn, lead to shortening of *C. elegans* lifespan. The stock solution of nanoparticles was resuspended homogenously before addition to the heat-killed bacterial culture.

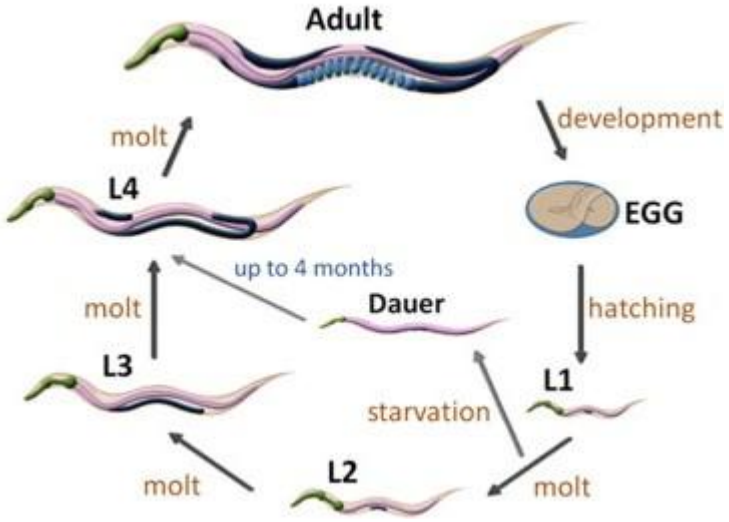


Figure 14 Lifecycle of *C. elegans*[222].

3.4.8.1 Feeding rate assay

The experiment was performed with five individual adult *glp-4* mutant worms were picked and transferred to assay plates for untreated control and treatment plates (50, 200, 500 and 1000 µg mL^{-1} graphene and PLA-6graphene) followed by incubation at 25 ˚C. The pharyngeal

pumping rate of five individual worms were counted for 5 sec using an Olympus CX21 compound light microscope under 10x magnification at 4, 24, 48 and 72 h post-exposure to nanoparticles. The total number of pumps was recorded in 5 sec. A pharyngeal pump was strictly defined as a complete backward movement of the terminal bulb grinder. The evaluation was repetitive for three times independently.

3.4.8.2 Lifespan assay

The experiment used adult worms which are were synchronised through a mixed population of *glp-4* mutants and the eggs were incubated at 25 °C for 72 h until the worms are fully grown into the adult stage. Later thirty individual adult worms of *glp-4* were picked manually and transferred to NGM plates. These plates are seeded with heat-killed E. *coli* OP50 in the presence and absence of graphene and PLA-6graphene. Later the plates were stored at 25 °C. The evaluation of live and dead worms was measured for every two to three weeks using Nikon SMZ 745 microscope until all the population of worms were found dead. The measurement was performed in triplicate and repeated independently for twice.

3.4.8.3 Reproduction assay

This experiment was performed using fertile wild-type N2 hermaphrodite worms. N2 adult worms of five individuals were picked and transferred to both control and nanocomposite treated assay plates (50, 200, 500 and 1000 µgmL^{-1}), followed by incubation at 25˚C. Later on the second and third day, five original adult worms were relocated to a new plate while leaving the eggs on the plates to grow and develop into the L3/L4 larval stage. After that, the number of children produced by the five worms were calculated using a Nikon SMZ 745 microscope. The assay was repeated independently for three times.

Chapter 4

A co-precipitation route for high yield synthesis of boron nitride nanotubes (BNNTs) and production of BNNTs-graphene by liquid phase exfoliation

4.1 Synthesis of high yield BNNTs

In this study, the synthesis was carried out at two different temperatures, 800 °C and 1200 °C under both ammonia and N_2 gas as per procedure.Figure 15 (a) showed the BNNTs obtained in powder form in an aluminium crucible after the annealing process at 800 °C. Figure 15(b) showed the BNNTs obtained at 1200 °C. At atemperature of 800 °C, the BNNTs obtained were partially developed with theexistence of other materials. While at atemperature of 1200 °C the BNNTs obtained were fully developed. Initially, it can be identified through colour variation of produced BNNTs after annealing at temperatures of 800 °C and 1200 °C as shown in Figure 15(a) and (b). However, the significant differences were identified through the structural analysis which was explained in the following section. BNNTs obtained at 1200 °C were used for all other experimental procedures in this study.

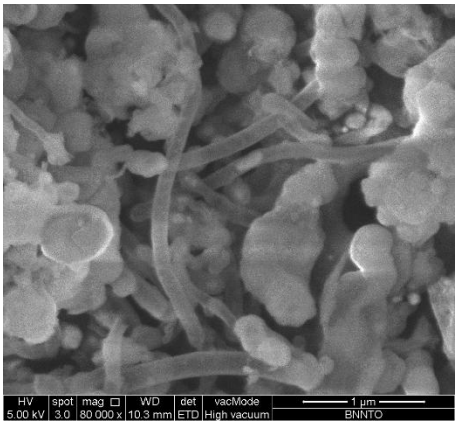
Figure 15 BNNTs produced under ammonia and nitrogen gas atmosphere at temperatures (a) 800 °C and (b) 1200 °C.

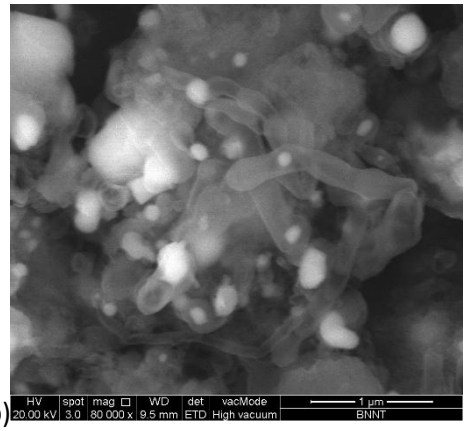
4.2 Morphology

4.2.1 BNNTs

The SEM images of the products synthesised at 800 °C and 1200 °C are shown in Figure 16(a) and (b), respectively. At 800 °C, it was observed that the presence of nanotubes along with other particles while the product of synthesised at 1200 °C consists of nanotubes only. Figure 16(c) clearly revealed that the nanotubes have smooth surfaces. The diameters of nanotubes range from 20 to 140 nm with an average value of 85 nm. Furthermore, it can be found that nanotubes were capped with particles at the ends (indicated by red arrows) as shown in Figure 16(d). The presence of the particles was considered as a representative symbol of vapour-liquid-solid (VLS) growth for the nanotubes.

Figure 17 illustrates the EDX spectra of BNNTs. For the temperature at 800 °C shown in Figure 17(a), there was a trace of impurities of Fe which were unreacted during the annealing process. However, at 1200 °C, only the existence of B and N showed in Figure 17(b). Both EDX spectra indicated no carbon signals, which specified the carbon-free nature of the produced BNNTs. The presence of the O peak might be due to the oxygen absorption transferred through the air during the formation of BNNTs. Therefore, it can be assumedthat the nanotubes were mostly composed of B and N.

(a) 

(b) 

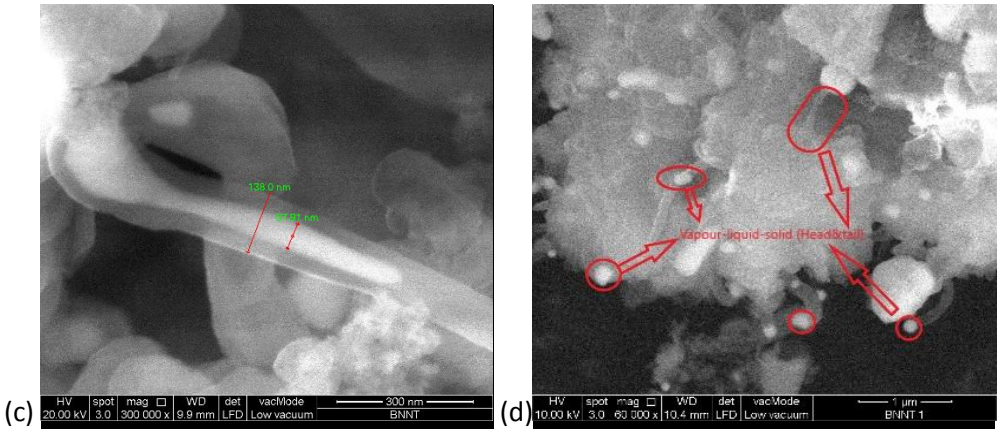


Figure 16Figure 3 SEM images of (a) BNNT annealed at 800 °C at 80,000X magnification, (b) BNNT annealed at 1200 °C at 80,000X magnification, (c) at high magnification, (d) vapour-liquid-solid (VLS).

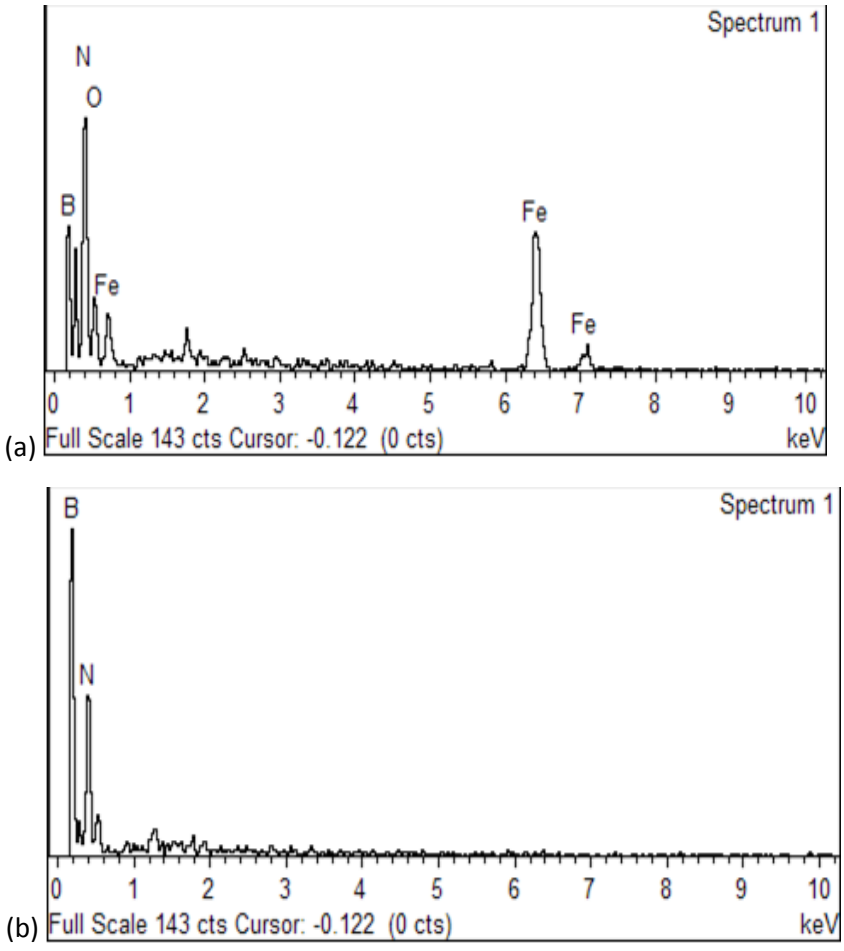


Figure 17 EDX spectra of BNNTs (a) at temperature of 800 °C, (b) at temperature of 1200 °C.

4.2.2 BNNTs-graphene nanohybrid

Figure 18 (a) showed the morphology of the graphene produced by Hummer's method. It revealed the many free-standing and ultrathin sheets of graphene. The SEM image of BNNTs-graphene was shown in Figure 18(b). It can be seen the layers of graphene were overlapped with BNNTs, but they were moderately transparent and the surface of the grid at bottommost could be seen effortlessly. Accordingly, it disclosed that layers were relatively thin.

Figure 18(c) represented the EDX spectra analysis of the surface of the hybrid. The presence of B, N and C were detected along with very less amount of Fe. Hence, it confirmed the layers were combined with graphene and BNNTs.

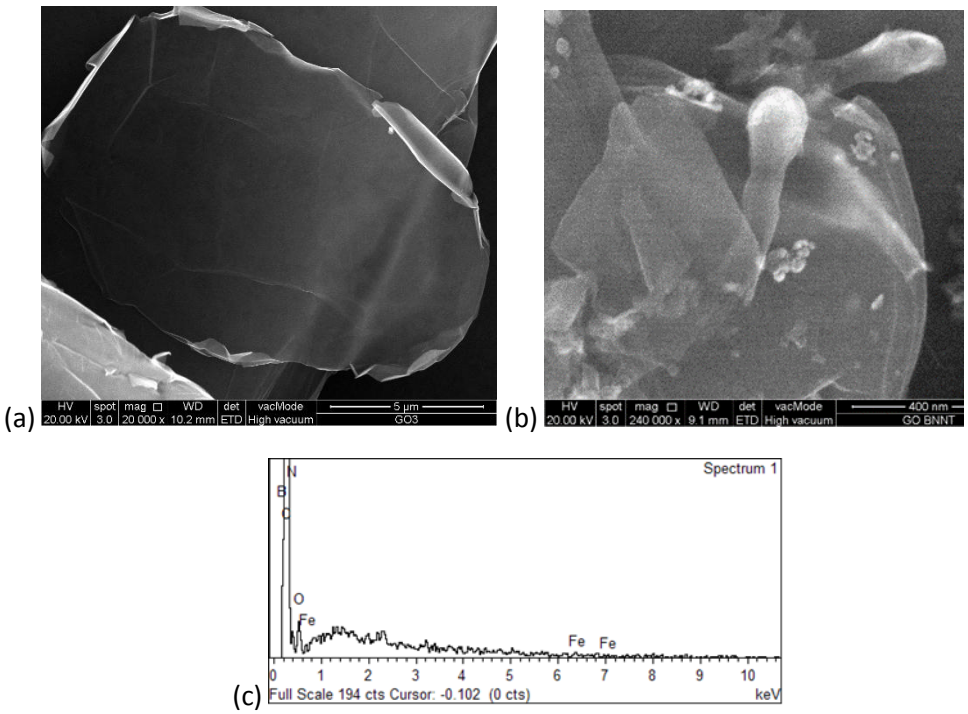


Figure 18Surface morphology of (a) Pure graphene produced through Hummer's method (20,000X magnification), (b) BNNTs-graphene (240,000X magnification), (c) EDX spectra analysis of produced BNNTS-graphene hybrid.

4.3Analysis of surface area of BNNT and BNNTs-graphene

The BET model was adopted to measure the surface area in mesoporous range (2-50 nm) based on the nitrogen gas absorption of the BNNTs and BNNTs-graphene. Table 1 showed the surface area of BNNTs and BNNTs-graphene hybrid. The surface area of synthesised BNNTs was 2.16 m^2 g^{-1}. According to Amada L. Tiano et al., the surface area could be increased with thepurification of nitric acid. The BNNTs-graphene surface area was 15.69 m^2 g^{-1}, which showed in the improvement of the surface area[254]. The better surface area can theoretically be recognised to the removal of impurities and exfoliated the layers of BNNTs-graphene during the acid treatment. Thus, it was mandatory to remove the impurities in the BNNTs and BNNTs-graphene for structural applications.

Table 4Surface area measurements produced by BET of BNNTs and BNNTs-graphene

Sample	**Surface area (m^2g^{-1}) via multipoint BET**	**Absorption average pore width (4V/A)**	**Desorption average pore width (4 V/A)**
BNNTs	2.16	304.7941 Å	306.5410 Å
BNNTs - graphene	15.69	179.85 Å	181.79 Å

4.4 Phase identification of BNNTs

Figure 19 showed the XRD patterns of the BNNTs obtained at two different temperatures,i.e., 800 °C and 1200 °C.The crystalline peak obtained at atemperatureof 800 °C, showed the highest peak at 45°. There were other peaks presented in the heat oftreatment at 800 °C which were attributed to theimpurities. According to Xiaofan Bi et al. the co-precipitation and annealing process carried out below 1000 °Cresulted in FeB and Fe phases other than obtaining pure

BNNTs[251]. While at atemperatureof 1200 °C the highest peak wasat presented 26.63°.Thatresultedin a purity of BNNTs.This pointed out that the nanotubes primarily consist of BNNTs, which were tubular structures formed out the raw materials like B, $(Fe(NO_3)_3.9H_2O)$ and $(CO(NH_2)_2)$[255]. The absence of any other prominent peaks in the XRD pattern suggests no chemical impurities in BNNTs produced at atemperature of 1200 °C.

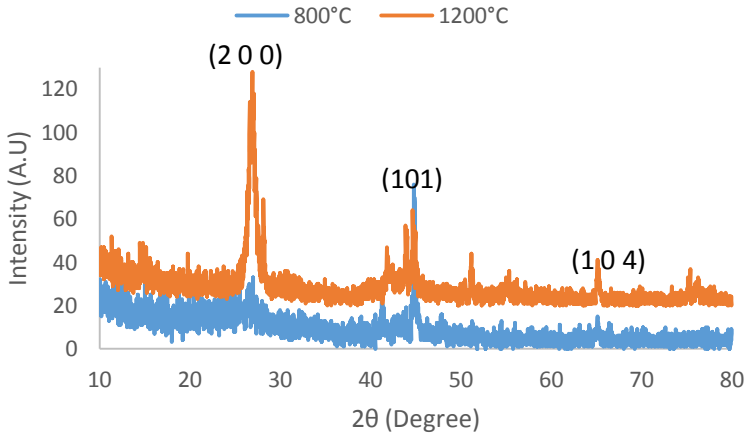


Figure 19XRD pattern of synthesised BNNT at 800 °C and 1200 °C.

4.5 UV- visspectrometer analysis of BNNTs-graphene

UV-vis spectrum of BNNTs-graphene is shown in Figure 20. The band gap energy of BNNTs was 5.67 eV at 280 nm. It is evidentaccording to properties of materials BNNTs have insulating and graphene has conductive characters[166, 252]. However, due to the limitation of the instrument, thewavelength was limited at 900 nm and it was not possible to observe the absorption peak of graphene, which is after 1000 nm according to O.Guler et al.[256]. There are no absorption peaks between 280 nm and 900 nmfor BNNTs-graphene hybrid. According to previous study,[256] the absorption peak of hybrid nanosheets of hexagonal graphene and hexagonal boron nitride was obtained at 1012 nm. Thus, it was predicted that the prepared BNNTs-graphene could absorb more light than BNNTs and graphene. The weight of the suspension form of BNNTs-graphene in the solvent DMF

was quite low. Correspondingly, thicker layers tended tosettle down in the liquid gently. To overcome the problem, the absorption test was carried out immediately after this suspension was sonicated for 1 h.

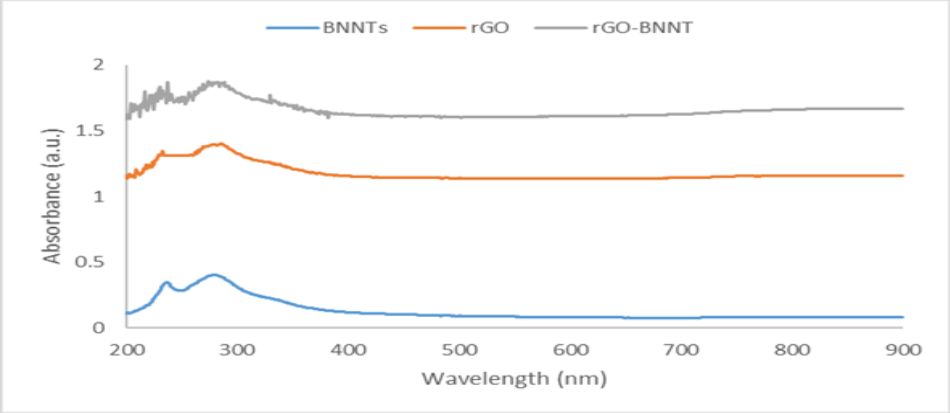


Figure 20UV-vis analysis of BNNTs, graphene, BNNTs-graphene.

4.6 Summary

The production of BNNTs through co-precipitation and annealing process was executed successfully. The morphology revealed the nanotubes in bamboo-shaped with an average diameter of 85 nm. Also, it was known that high temperature is favourable for the growth of thick BNNTs which were bamboo-shaped while the temperature below 1000 °C resulted in partially developed nanotubes. Additionally, hybrid containing BNNTs and graphene was successfully prepared by liquid phase exfoliation method. The SEM images showed the layer of nanotubes mixed well with graphene layers. Moreover, the absorption character of the hybrid was shown due to the presence of boron. The hybrid can be applicable in electronic and mechanical applications such as supercapacitors, solar energy harvesting.

Chapter 5

Characterization of boron nitride nanotubes (BNNTs) reinforced polycaprolactone (PCL)

This chapter discusses the mechanical, structural and thermal properties of the PCL-BNNTs prepared by solvent mixing method. The pure PCL, PCL-2BNNTs and PCL-5BNNTs were characterised using SEM, densitometer, TGA and tensile test.

5.1 Density

The density of pure PCL, PCL-2BNNTs and PCL-5BNNTs was measured by using adensitometer. Pure PCL showed lower density than the PCL-BNNT composites. The measured densities at temperature of 35 °C for PCL, PCL-2BNNTs and PCL-5BNNTs were 1.125, 1.237 and 1.438 g ml^{-1} respectively. The specific gravity of the PCL, PCL-2BNNTs and PCL-5BNNTs were 1.136, 1243 and 1.446 g ml^{-1} respectively. The density and specific gravity of PCL increased with increasing theamount of BNNT in the PCL.

5.2 Surface Morphology of PCL-BNNTs composite film

Morphological analysis is very important for the evaluation of the dispersion condition of the filler in the polymer matrix. SEM images of the cross-section of the neat PCL, PCL-2BNNTs and PCL-5BNNTs were shown in Figure 21. The neat PCL showedmore pores as shown in Figure 21(a) compared tothe PCL-2BNNTs and PCL-5BNNTs. The dispersion of BNNTs in PCL was enabled in the solution with an outcome in a solid assembly. The processing parameters of the neat PCL and PCL reinforced with BNNTs were the same, the change in porosity was caused by the presence of BNNTs filler in the PCL matrix.Figure 21(b) represents the presence of BNNTs in the PCL matrix with an averagediameter of 85nm. Figure 21(c) showed the fracture surface of PCL-BNNTs where the BNNTs acted as

abridge[214] connecting thelayers of PCL (indicated by black arrows). BNNTs acted as rigid reinforcement in strengthening the polymer nanocomposite. The homogenous dispersion of BNNTs in PCL was due to helical structure of the polymer, that likely to form a coil thus covering the BNNTs and lead a robust π-π interaction [149, 215].

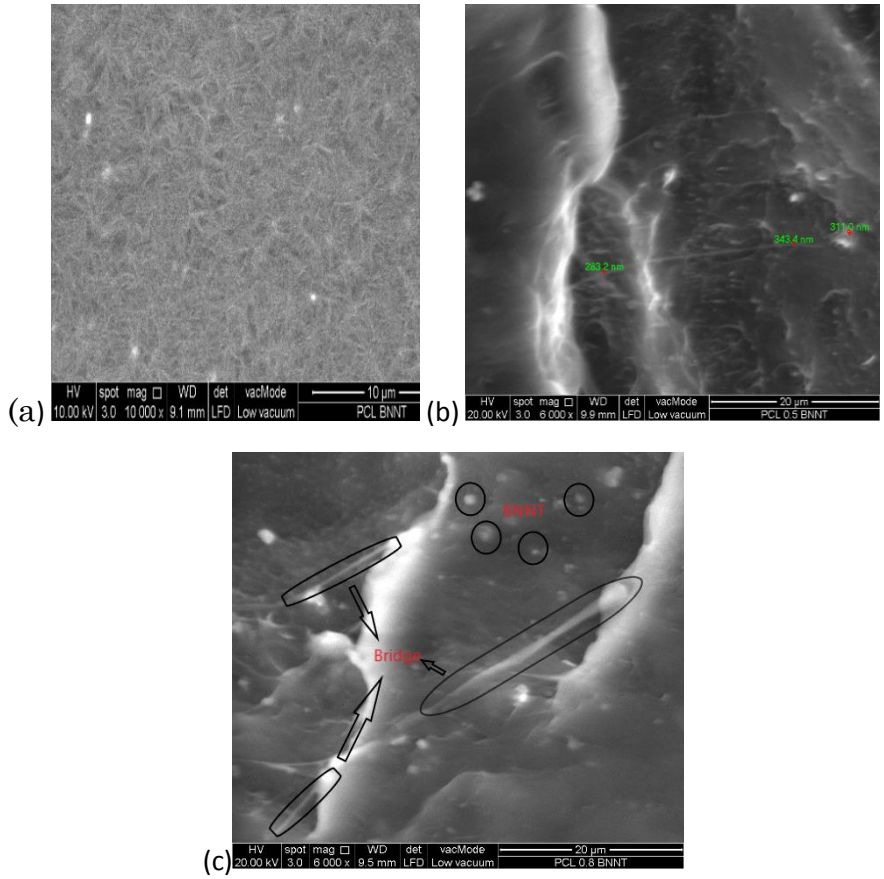


Figure 21SEM images of cross-section of (a) neat PCL (at 10,000 X magnification), (b) PCL-2BNNTs (at magnification at 6000X), (C) PCL-5BNNTs (at magnification at 6000X).

5.3 Thermogravimetric analysis

The thermal stability of the BNNT, PCL, PCL-2BNNT, and PCL-5BNNT were examined in the temperature range of 25 to 800 °C. The TGA graphs of neat BNNTs, pure PCL, PCL-2BNNTs and PCL-5BNNTs were shown in Figure 22 . There was no significant weight loss in BNNTs throughout the heating process, which represented by the straight line in the graph. The pure PCL has a thermal

decomposition between 350 to 450 °C. At 450 °C, almost 50% of PCL polymerwas decomposed. However, due to the presence of BNNTs there were still 1% to 4% residues of PCL-2BNNTs and PCL -5BNNTs exists.

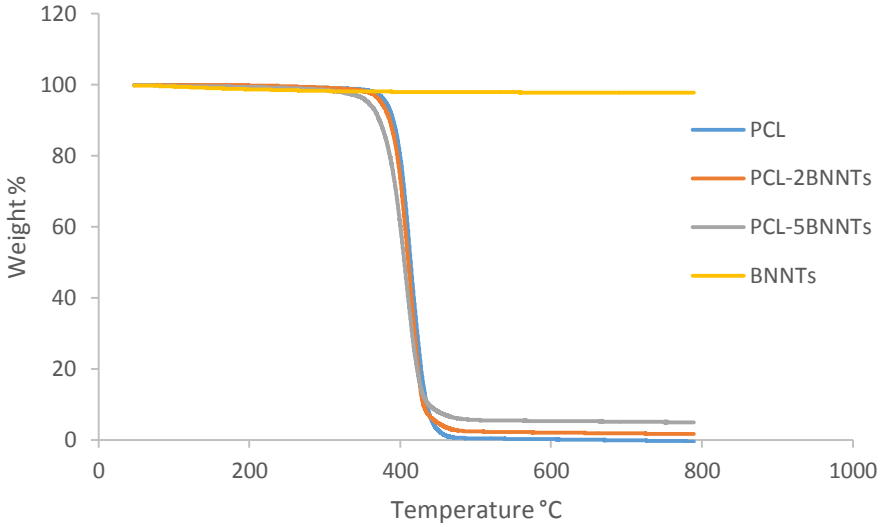


Figure 22TGA analysis of PCL-BNNTs nanocomposites.

5.4 Tensile test

Figure 23 showed the engineering stress-strain behaviour for PCL and PLC–BNNTs composite films up to a strain of 3.5 (350% elongation), obtained from the uniaxial tensile tests. The gauge length of the tensile sample was 5 mm. the maximum cross-head movement possible being 12 mm.The strain value wasrestricted up to 3.5. Stress-strain behaviour indicated a gradual increase in the tensile strength with the addition of BNNTs from 1.45 MPa in PCL to 3.59 and 4.35 MPa for PCL–2BNNTs and PCL–5BNNTs, respectively. Tensile strength at 3.5strain increased by 85 % and 101 %, with theaddition of 2 and 5 wt% BNNTs into polymer, respectively. The specimens resumed back to their original shape without any noticeable bend after a maximum strain of 3.5 was achieved. Addition of the second phase of a flexible matrix frequently displayed a damaging effect on its deformability. This negative effect turned into more noticeable where the matrix was a flexible polymer such as PCL. But in PCL–BNNTs composite films, even with theaddition of BNNTs, the deformability of the PCL is not

affected up to 350 % elongation. Such behaviour was attained due to the high flexibility of BNNTs [258].

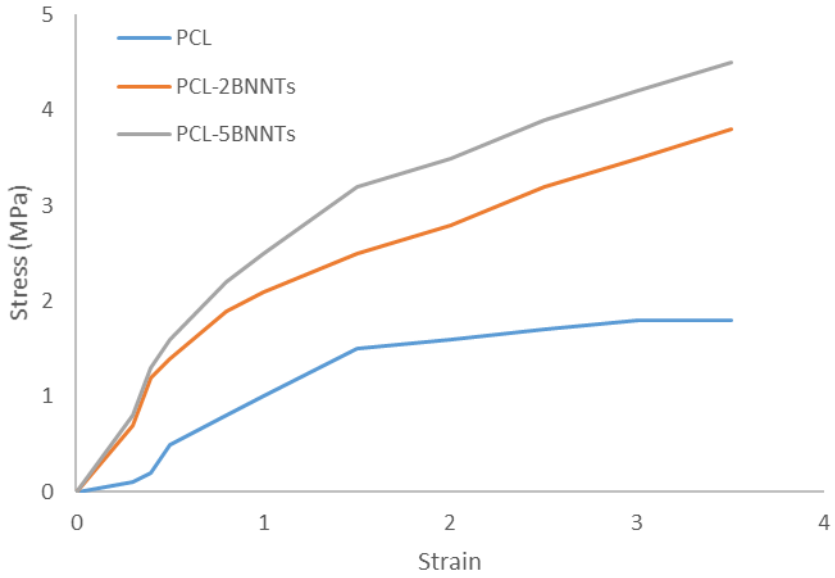


Figure 23Tensile stress-strain curve for the PCL, PCL-2BNNTs and PCL-5BNNTs composite films.

5.5 Summary

PCL-BNNTs composites films with enhanced mechanical and thermal properties have been prepared efficiently for their possible applications in the electromechanical and biomedical fields. PCL-5BNNTs displayed impressive improvement in the tensile strength about 4.98 MPa without having any contrary effects on elastic modulus. The even dispersion and adequate interfacial bonding between the BNNTs filler and PCL matrix attributed the excellent mechanical and thermal properties.

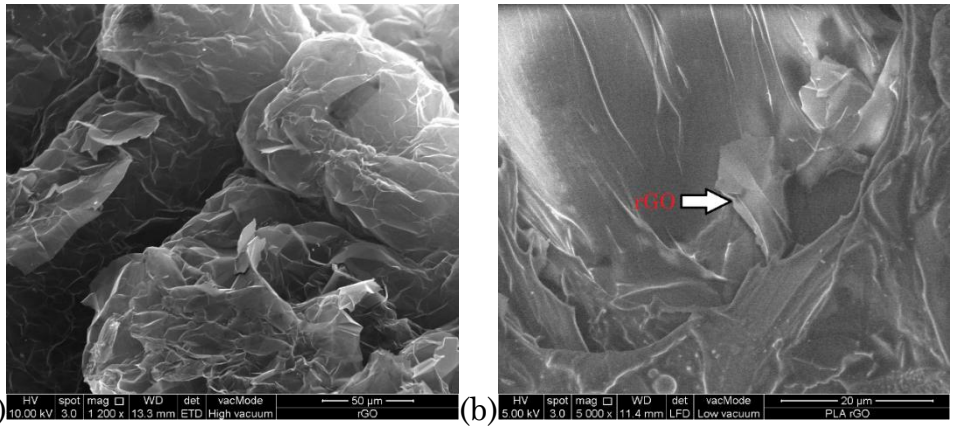
Chapter 6

Toxicity evaluation of graphene and poly(lactic-acid) using a nematode model

This chapter discusses thebiocompatibilityresults of PLA-graphene polymer nanocomposite. The preparation process of polymer nanocomposites carried out through the solvent mixing process, which was explained in the section 3.3.1. The graphene and PLA-graphene were used for analysis of structural and in vivo assessment of polymer nanocomposite performed on *Caenorhabditiselegans (C. elegans)*. The biological effects such as feed rate, lifespan and reproduction were validated through a 1mm long nematode as a model living system known as *C. elegans*.

6.1 Morphology

The typical structures of graphene with wrinkles, fully exfoliated, ultrathin layers were observed by SEM microscopy as depicted in Figure 24(a). The dispersion of graphene sheets in the PLA matrix was homogeneous. It can be seen in Figure 24(b) that graphene sheets were fully exfoliated and well dispersed in PLA matrix (as indicated by arrow). The graphene sheets were coated with PLA, displaying the actual interfacial interactions between the graphene sheets and PLA chains [252, 259]. Additionally, it has also been observed that there was no agglomeration on the fracture surface.



(a) (b)

Figure 24SEM images of (a) neat graphene(at magnification 1,200X), (b) PLA-graphene (at magnification 5,000X).

6.2 Toxicity evaluation

6.2.1 Feed rate assay

*C. elegans*were treated with both graphene and PLA-graphene portrayed in the Figures 25(a) and 25(b) respectively. The pharyngeal pumping was done from 4 to 72 h (p>0.05, n=15) and there were no notable changes in the worms witnessed during the process. The pumping rate in untreated control plates was comparatively persistent throughout the complete experiment with an average pump of 18.7 – 20.2 and 18.8 – 23.1 from 4 to 72 h for graphene and PLA-graphene, respectively. For neat graphene-treated worms, the pumping rate was 15.6 – 20.3, while for worms introduced to PLA-graphene, the median pump was 16.4 – 22.7 pumps per 5 sec. The uptake of food by *C. elegans* indicatesby the pharyngeal pumping rate and the data indicates the exposure to graphene and PLA-graphene did not affect the intake of food by *C. elegans*[231]. Thus it was suggested that the graphene and PLA-graphene are not toxic to worms.

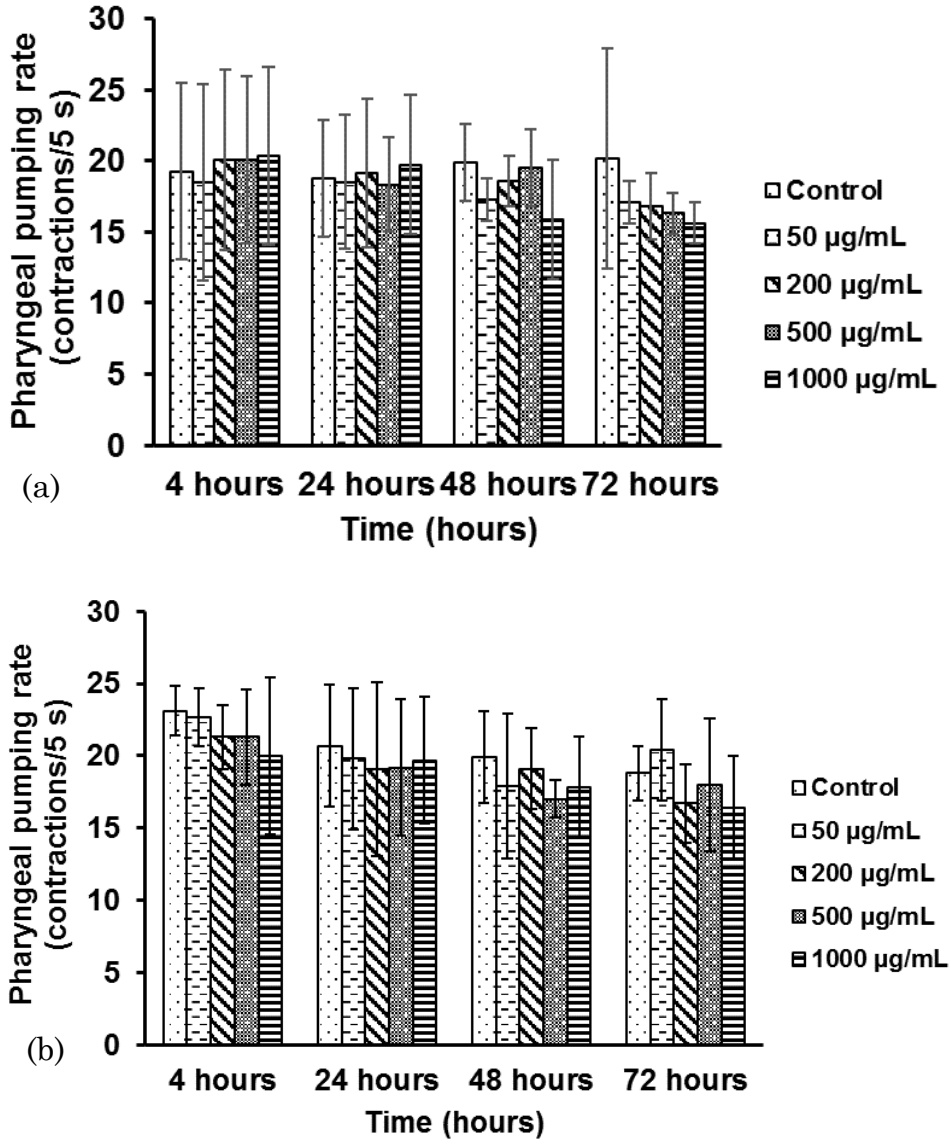


Figure 25The Pharyngeal pumping rate of worms in 5 sec upon exposure to 50, 200, 500 and 1000 µg mL-1 (a) graphene and (b) PLA-graphene for 4, 24, 48 and 72 h. The error bars represent the standard error of the mean of each mean value. Data shown are a combination of three independents experiments.

6.2.2 Lifespan assay

When the worms were fed with food source containing graphene and PLA-graphene, all the treated and untreated worms were able to stay alive up to 13 to 18 days, respectively. There was no noteworthy variation between the lifespan of worms introduced to graphene (Figure 26(a)) and PLA-graphene (Figure 26(b)) as compared with the untreated control population (p>0.05, n=40)[219].

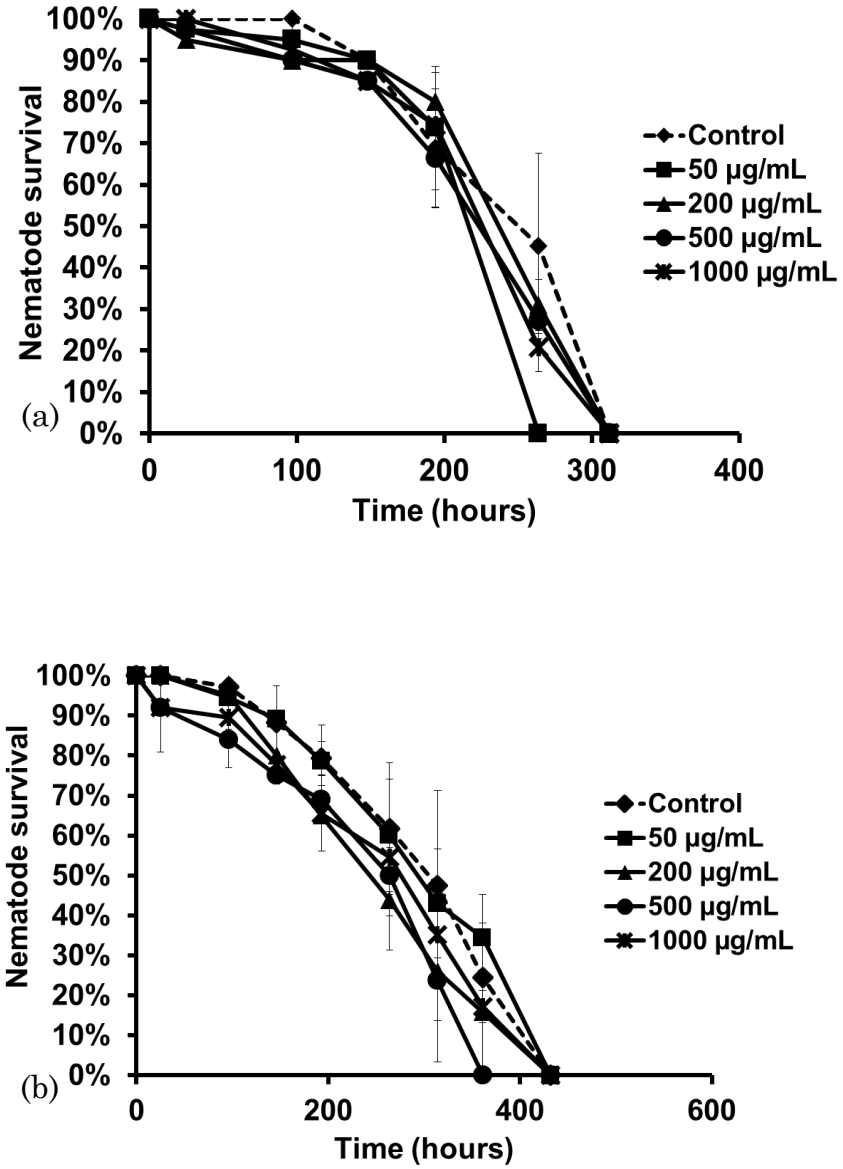


Figure 26 Lifespan of worms fed on their natural food source E. *coli* OP50 supplemented with 50, 200, 500 and 1000 µg mL^{-1} (a) graphene and (b) PLA-graphene. The error bars represent the standard error of the mean of each mean value. Data are presentative of two individual experiments.

6.2.3 Reproduction assay

Nematode exposed to graphene exhibited no significant changes in the number of offspring per adult compared to control, regardless of concentration (p<0.05, n=15). The data of progeny produced is shown in Figure 27. Hence it indicates that the exposure to graphene up to 1000 µg mL^{-1} did not affect the reproductive ability of the worms.

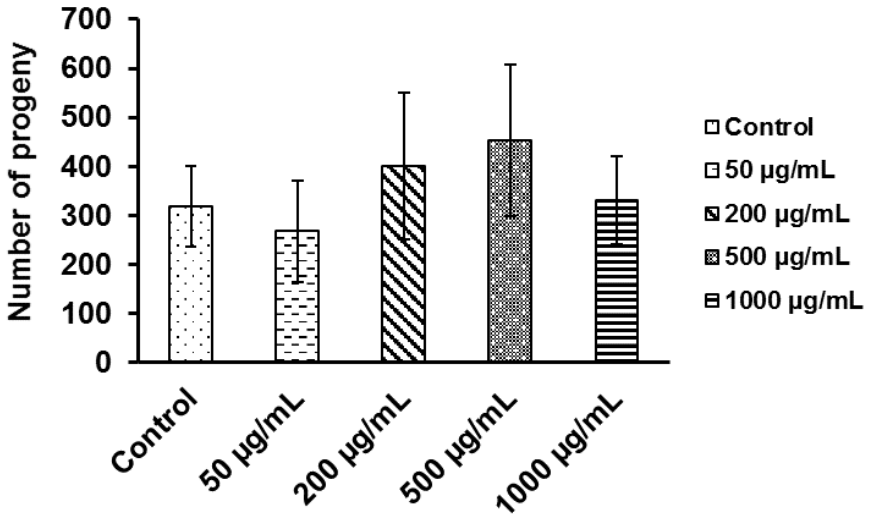


Figure 27Total number of progeny produced upon exposure to 50, 200, 500 and 1000 µg mL^{-1} graphene.

6.3 Summary

Biocompatible polymer nanocomposites and nanoparticles have the great potential in the topics of biomedical such as drug delivery and tissue engineering because of their unique physiochemical properties. However, many of nanocomposites materials have been found to be toxic. It is vital to investigate the effect of materials on the biological system before they are being mixed into any consumer products. In this study, both graphene and PLA-graphene did not exert an adverse effect on the pharyngeal pumping rate, lifespan and reproduction rate of *C. elegans*. Thus, it is recommending that graphene and PLA-graphene were not toxic to a living organism. Consequently, the materials are safe to living organism at a concentration up to 1000 µgmL^{-1}.

Chapter 7

Conclusion and Future work

7.1 Conclusion

In the current study, initially, the synthesis of BNNTs through co-precipitation and annealing process has been successfully achieved. It was evident that the vast quantities of pure BNNTs can be acquired at a high-temperature range. The nanotubes synthesised at 1200 °C displayed bamboo-shaped structures with an average diameter of 85 nm. Furthermore, synthesis of graphene through Hummer's method and reduction process was performed which results in obtaining ultrathin layers of graphene sheets with high purity. Secondly, the combined hybrid structure of BNNTs-graphene hybrid production was magnificently attained by using liquid-phase exfoliation method. The SEM results obtained depictedboth of thenanomaterials intercalated and developed a hybrid nanostructure.

Thirdly, PCL-BNNTs polymer nanocomposites were prepared by solvent mixing procedure. The nanocomposite films of PCL-BNNTs showed an improved mechanical and thermal properties. The homogenous mixture of PCL matrix with BNNTs filler was attained and it was observed in the fracture surfaces of polymer composites by using morphological results. The strength of PCL incorporated with higher rate BNNTs exhibited an improvement in tensile strength without showing any negative effects on elasticity. Thus, these are attributed to the uniform dispersion and good interfacial bonding of BNNTs with the polymer matrix.

Finally, toxicity evaluation of graphene and PLA-graphene was efficiently done through *C. elegans*. The complete data from an in vivo whole animal model specifies the graphene and PLA-graphene biocompatibility. It was found no detectable toxicity in*C. elegans* on the feed rate, lifespan and reproduction capacity. Hence it was suggested

that these materials are safe to theliving organism atto the concentration of 1000 μg mL^{-1}.

7.2 Future work

- Since the study of hybrid integrated PLA matrix was not involved, it was recommended to carry out the preparation of hybrid BNNTs-graphene hybrid polymer nanocomposites to investigate the mechanical and thermal properties.
- Furthermore, it was suggested to study the toxicity assessments of PCL-BNNTs through *C. elegans*. This helps in applications of tissue regenerations which is a current growing topic in the biomedical field.
- Consequently, graphene and PLA-graphene did not show any toxicity. It is recommended to carry out the cell culture, gene expression and cell viability for tissue scaffolding for the future research studies.

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