General Introduction

Highlights

Fundamentals of waterborne hyperbranched polyester nanocomposites are discussed in this chapter. It includes a brief description of polyesters with different structural architectures. The materials and methods for obtaining such nanocomposites are demonstrated. The nanocomposites of such polymers with different nanomaterials especially graphene oxide and carbon dot are also highlighted. Various analytical, spectroscopic, diffraction and microscopic techniques such as NMR, XRD, FTIR, TGA, DSC, SEM, Raman, TEM, etc. used for characterization of such materials are briefly demonstrated, herein. The influence of nanomaterials on the performance including physical, mechanical, thermal, optical, biological, etc. of pristine polyesters is also discussed. The focus is also paid to highlights some unique properties like anti-icing, anti-fogging, anti-reflecting, self-cleaning, etc. of such nanocomposites. This chapter further highlights the applications of waterborne polyester nanocomposites in various advanced fields. Lastly, the scopes, objectives, and plan of the present investigation are stated in this chapter.

1.1. Introduction

Polymeric materials are designed to meet the service demands for their end applications. They are utilized in almost every sphere from daily life consumable items to smart biomedical devices, owing to their exceptional favorable attributes [1]. However, most of the polymeric materials are obtained from petroleum resources, which are non-renewable, and they cause a significant amount of greenhouse gases generation to the environment. Thus, the limited abundance of petroleum resources and the adverse effects to the environment created a huge demand for alternative renewable resources to replace the former [1]. Further, depletion of fossil fuels and adverse impact of non-biodegradable synthetic polymers to the environment inclined the scientists to develop biodegradable polymeric materials from renewable bio-resources, so that the environmental pollution caused by so-called plastic waste can be minimized [2]. Indeed the utilization of such renewable resources is gaining great attraction both in academic and industrial domains, in recent times, particularly in energy and material sectors [3, 4]. Again, in material fields, polymeric materials occupy the most decent position for their inherent favorable characteristics. Further, chemical structure along with architecture is the most critical issue of polymers in addition to their molecular weight. In this context, three-dimensional architectural dendritic polymers with densely branched structure enjoy the advantages of high solubility, low viscosity, a large number of surface functionality, high reactivity, etc. over conventional linear analogous polymers [5]. Dendrimers and hyperbranched polymers are the two kinds of such architectural macromolecules, where the later are relatively inexpensive as they are easy to synthesize in large quantity through simple methods, unlike dendrimers. Therefore, bio-based biodegradable hyperbranched polymers may be considered as an alternative to petroleum- based linear polymers [5]. Again, a considerable amount of volatile organic compounds (VOC) are released into the air during preparation and application of conventional solvent borne polymeric systems, which are responsible for the increase in environmental pollution and health problems. Thus, to address this shortcoming, development of waterborne polymeric systems is considered as a good alternative, as advantageous features like minimum or no VOCs, non-flammability, no odor, environmentally friendly, non-toxicity, and simple to clean up can be achieved from such systems [6, 7].

Further, among different types of bio-based polymeric materials, polyesters are the most promising members owing to their fascinating attributes like biocompatibility, physical and chemical (except alkali) stability, ready availability, comparatively low cost, etc.[8]. Further, such polyesters with aliphatic structures have a little environmental impact upon disposal as they can offer most desirable feature like biodegradability [9]. Also, the bio-based reactants like di/polybasic acids and di/polyols used for the synthesis of polyesters are relatively easy to access from renewable bio-resources, compared to others like olefins, diamines, isocyanates, etc. In addition, such polyesters have broad spectrum of applications in the fields of surface coating, biomedical, adhesive, paint, laminate, packaging, etc. [8, 9]. Therefore, bio-based aliphatic waterborne hyperbranched polyesters (WHPE) may be an excellent alternative to their analogous conventional petroleum-based polyesters, as the former can also follow the tenets of Green Chemistry [10].

However, such bio-based polyesters suffer from inherent drawbacks like poor mechanical strength, low hardness and weak alkali resistance which limit their applicability in many advanced fields [11]. In this milieu, the incorporation of nanomaterials (better than conventional micro reinforcing agents) into the polyester matrices not only addresses the above drawbacks but also imparts some exciting properties which widen the applicability of such resultant systems [12]. Thus, the development of polymer nanocomposites, where at least one phase must be in nanometer scale, is one of the most intelligent ways to enhance the performance of such polymers and thus fascinated a great deal of attention from the material scientists and industrial community [13]. In this vein, different types of nanomaterials including zero-, one- and two-dimensional such as nanoparticles, nanotubes, nanowires, nanosheets, nanolayers, etc. are explored in polyester nanocomposites [12-15]. Raju *et al.* [13] reported the fabrication of ZnO-based polyester nanocomposite and showed enhancement in mechanical properties. Further, clay-based polyester thermosetting nanocomposite with good thermal, mechanical and rheological behaviors was reported by Bharadwaj *et al.* [16]. Ghanem *et al.* [14] fabricated TiO_2-based hyperbranched polyester (HPE) nanocomposite by both *ex-situ* and *in-situ* techniques and studied their photocatalytic activity. Furthermore, HPE nanocomposite was fabricated by Zhao *et al.* [12] using ZnS nanoparticles and exhibited high refractive index. Again, recent times, carbon-based nanostructures are much discussed in nanotechnology owing to their distinctive combinations of physical, chemical, thermal and electrical properties and hence used in different fields including biomedical, energy storage, photocatalytic, etc. [17]. Graphene is one of the most important members of the carbon nanomaterial family, enjoying analogous optical, electrical, and thermal properties like carbon nanotubes (CNT), but the two-dimensional atomic-sheet like structure of graphene facilitates structurally strong yet extremely flexible, which enables it as smart flexible and thin engineering materials with high performance [18]. In this milieu, graphene oxide (GO)-based polyester nanocomposite with excellent mechanical properties was reported by Bora *et al.* [19]. However, waterborne polyester/GO nanocomposite is not found in the literature. One of the fascinating carbon nanostructural water-soluble (nano-level) nanomaterials is carbon dot (CD) which shows peculiar but interesting photoluminescence (PL) properties [20]. Nitrogen-doped CD-based poly(urethane-urea) nanocomposite was fabricated by an *in-situ* technique. The poly(ester amide)/CD nanocomposite was used for the synthesis of benzaldehyde through greener oxidation of benzyl alcohol in the presence of visible light. Further, Gogoi *et al.* [21] reported the fabrication of CD-based waterborne hyperbranched polyurethane nanocomposite and their biocompatible attributes. However, CD-based polyester nanocomposite is not found in literature, so far. Thus, high-performing bio-based biodegradable aliphatic WHPE nanocomposites with water-soluble carbon nanomaterials are not only interesting but also valuable, under the current scenario of advanced material development.

Thus, investigation of bio-based biodegradable aliphatic WHPE nanocomposites with GO, CD and their nanohybrids seem to be encouraging in various fields of applications as advanced sustainable polymeric materials and hence the subject matter of the present thesis.

1.2. Historical background

In the field of polymer science, the first work was on derivatization of the natural polymer, cellulose to celluloid and cellulose acetate, carried out by Braconnot along with Christian Schonbein in the 1830s. In 1833, the term "polymer" was coined by Jons Jakob Berzelius. Leo Baekeland in 1907 invented the first synthetic polymer called Bakelite through polycondensation reaction between phenol and formaldehyde. Hermann Staudinger first proposed the term macromolecules in 1922 and defined that polymers consist of elongated chains of atoms which held simultaneously by covalent bonds [22, 23].

However, polyester started its journey in 1847 when polyglycerol tartarate was obtained by the reaction between tartaric acid and glycerol, which was performed by

Barzelius. General Electric Co. had first established the film forming capability and properties of the condensation products of polybasic acids and polyhydric alcohols, during 1912-1915. While, the unsaturated polyester resin, glycerol maleates was developed by Vorlander in 1894. In 1901, W. J. Smith synthesized poly(glyceryl phthalate) by reacting phthalic anhydride with glycerol. In 1933, Kienle and Hovey published a US patent (US1893873) on oil-modified polyester resins. However, in 1939, a polyester fiber called Terylene was first produced by a group of British scientists [24, 25].

Again, hyperbranched polymers were first introduced from a theoretical viewpoint in 1952 by P.J. Flory. In late 1980 DuPont researchers, Kim and Webster established the single-step polycondensation process of AB_2-type monomers to obtain dendritic macromolecules, and they coined the term “hyperbranched polymers”. Hyperbranched polyphenylene was the first such polymer and appeared in a patent in 1987 [26, 27]. However, aliphatic HPE of dimethylol-propionic acid and different polyols were first reported in 1993 [28]. In 2004, the synthesis of bio-based HPE from adipic acid and glycerol was reported by Stumbe and Bruchmann [29] using the tin catalyst. HPE of 2,2-bis(hydroxymethyl) propionic acid (bis-MPA), pentaerythritol, trimethylol propane, or glycerol were synthesized in 2007 [30].

On the other hand, in 1998 UV-curable waterborne unsaturated polyesters were developed for wood coatings application [31]. While in 2003, Asif and Shi [32] had synthesized WHPE of a polyhydroxy-aliphatic polyester core, Boltorn™ H20 (with 16 hydroxyl groups) with an end-capped salt-like structure under UV irradiation. However, partially renewable resource-based waterborne polyester was first reported from bio-based isosorbide, non-renewable maleic anhydride, and PEG in 2010 by Jasinska and Koning [33].

Again, polymer nanocomposite came to exist commercially as well as academically since 1980’s though the term was coined by Theng in 1970 [34]. In the late 80’s Toyota research laboratories had reported nanoclay (layered-silicate)-based nylon-6 nanocomposites with significant improvement in mechanical properties and heat deflection temperature. These materials were commercialized as belt covers for Toyota cars [35]. Many polyester nanocomposites have been developed by using different types of nanomaterials like CNT, nanofibre, clay, graphene, metal oxide nanoparticles, etc. and significant improvements in mechanical, electrical, thermal, gas barrier properties, etc. were observed. The fabrication of carbon nanofibre-based polyester nanocomposites and their enrichment in mechanical properties were reported by Ma *et al*. [36] in 2003. In 2008, Kim and Macosko [37] reported the fabrication of polyester nanocomposites using functionalized graphite sheets and demonstrated the enhancement of their mechanical properties. Lee *et al.* [38] in 2005 fabricated multi-walled CNT (MWCNT)-based polyester nanocomposite and gained significant improvement in mechanical and thermal properties.

1.3. Materials and methods

Different types of starting materials and preparative methods have been used for obtaining different polymers like polyesters, nanomaterials like GO and CD, and their nanocomposites. Some of the important such materials and methods are discussed in this section.

1.3.1. Materials

Almost all polymers and nanomaterials are utilized to produce various polymer nanocomposites. However, since the present thesis deals with polyester nanocomposites using GO, and CD and CD-based nanohybrids, so the discussion is mainly restricted to these materials.

1.3.1.1. Polyester

Polyester is most widely used synthetic polymer which has at least one ester linkage per repeating unit. It is the polycondensation product of a polybasic acid and polyhydric alcohol [10] (**Figure 1.1**). Thus, a large number of polybasic acids (**Table 1.1**) and polyhydric alcohols (**Table 1.2**) have been used for the synthesis of different polyesters. Along with the polybasic acid, monobasic acids like lactic acid, acrylic acid, glycolic acid, etc. have also been used to terminate the polymeric chain [39, 40, 41]. In addition, some aromatic polybasic acids and some anhydrides are also found to be used for the synthesis of varieties of polyesters (**Table 1.3**). Again, in order to obtain waterborne polyesters, reactants with polar functional groups like -COOH, -OH, -NH_2, etc. are necessary to use. In this milieu, bis-MPA is very useful and widely used not only because of the reactive carboxylic groups but also the tertiary carboxylic and hydroxyl groups remain in the structure after polymerization reaction, that help to provide water solubility [42]. In addition, this novel reactant is also used for the synthesis of HPE [43]. Further, poly(ethylene glycol) is also used as one of the reactants to achieve water solubility of the resultant polyester [33].

Bio-based acids

Different bio-based polybasic acids have been used for the synthesis of polyesters (T**able 1.1**). Carbohydrates derived dibasic acids, and monobasic acids are the most important reactants derived from biomass. Itaconic acid or methylene succinic acid is a promising precursor for a various chemical transformations owing to the presence of α,β-unsaturated double bond along with two carboxylic acid linkages. Although, it was first obtained by the thermal decarboxylation of citric acid, but now it is produced in industrial scale by fermentation of carbohydrates in presence *Aspergillus terreus*.

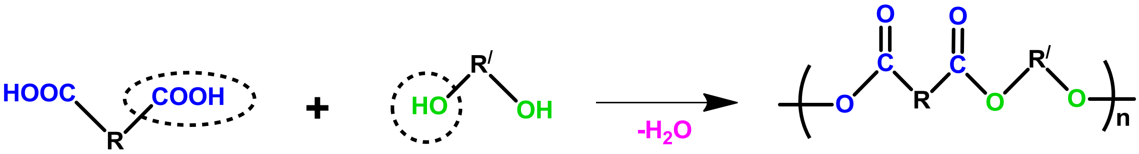
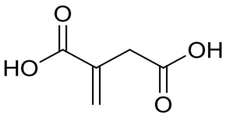
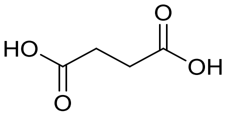
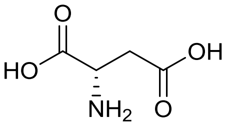
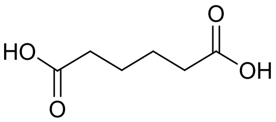
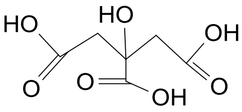
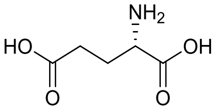
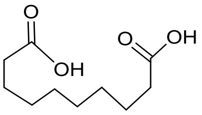
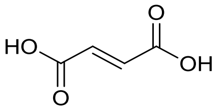
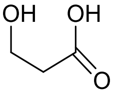
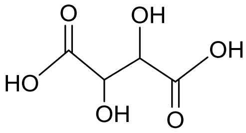
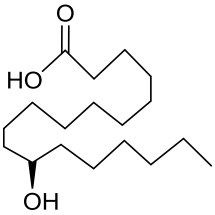
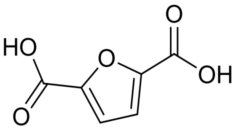
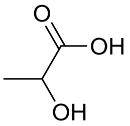
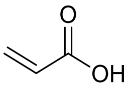
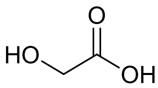
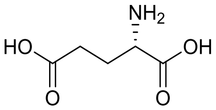


Figure 1.1: Formation of polyester by a polycondensation reaction

Table 1.1: Different polybasic and monobasic acids with their structures and applications

Type	Name	Structure	Applications
Aliphatic acids	Itaconic acid		Paper coating latexes, shape memory materials, thermal and UV curable coatings, etc.
	Succinic acid		Powder coating applications, biodegradable materials, etc.
	Aspartic acid		Drug delivery applications
	Adipic acid		HPE for antimicrobials, pesticides and pharmaceuticals
	Citric acid		Biodegradable, and biocompatible materials, tissue engineering scaffolds, etc.

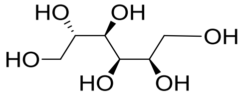
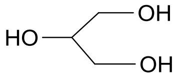
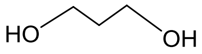
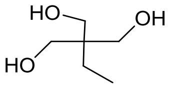
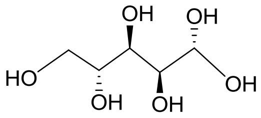
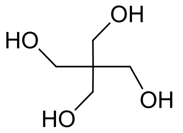
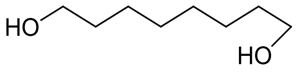
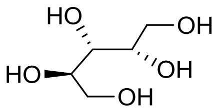
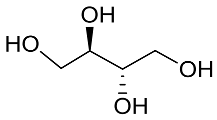
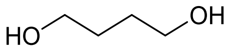
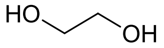
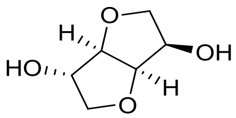
	Glutamic acid		Biomedical applications including drug delivery system, tissue engineering, etc.
	Sebacic acid		Provides hydrophobicity, biodegradability, biocompatibility, excellent flexibility and chemical resistance
	Fumaric acid		Biomedical applications
	3- hydroxy propionic acid		Biodegradable materials
	Tartaric acid		Biodegradable materials
	Ricinoleic acid		Provides hydrophobicity to the polymer, drug release, biodegradable materials
	2, 5 – Furan dicarboxylic acid		Biodegradable materials, good mechanical properties
Monobasic c acid	Lactic acid		Biomedical applications such as dental implants, sutures, stents, bone screws, pins vascular grafts, etc.
	Acrylic acid		Good cracking resistance, flexibility and thixotropic properties
	Glycolic acid		Drug release and tissue engineering scaffolds
	Glutamic acid		Biomedical applications including drug delivery system, tissue engineering, etc.

It offers flexibility to the polyesters with tuneable features and can be used as a substitute for acrylated polyesters. Thus, the polyesters derived from itaconic acid can be utilized in different applications like thermal and UV curable coatings, the main resource for paper coating latexes, emulsion paints, shape memory polymers, etc. [44, 10, 45]. Again, succinic acid, a bio-based dicarboxylic acid is obtained from biomass resources through fermentation in a commercial scale which signifies a breakthrough toward the development of a bio-based economy [46]. Further, adipic acid is available from glucose through catalytic hydrogenation of glucaric acid by following a two-step process [47]. Citric acid is another important multi-functional carboxylic acid monomer and reacts with alcohols or polyols to form polyesters with three- dimensional architectures. It can also act as a cross-linker, and such polyesters exhibited good biocompatibility. It is cost-effective, highly bio-friendly material, and can improve hydrogen bonding to the resultant polymer [48, 49]. On the other hand, sebacic acid prevents cyclization and offers hydrophobicity to the polymer. It can be entirely broken down into succinyl CoA and acetyl-CoA and thus enters into the Krebs' cycle [50]. It consists of a reactive double bond which can take part in chemical cross-linking reactions. The first and most exhaustively explored fumarate-based copolymer is poly(propylene fumarate), a biodegradable co-polyester [51]. Ricinoleic acid is a naturally produced fatty acid which is isolated from castor oil. The long hydrocarbon chain of ricinoleic acid acts as a plasticizer and influences the physical as well as mechanical properties together with the hydrophobicity of the polyesters [52]. One of the highly precious green building blocks used for the synthesis of aromatic polyesters is 2,5-bis(hydroxyl methyl)furan and it can be transformed simply from 5-hydroxymethylfurfural, obtained from carbohydrates. Its rigid furan structure can be retained in synthesizing polyesters and thus provides good mechanical properties and high glass transition temperatures (T_g) [9]. Its structure is similar to that of terephthalic acid, and thus it may be used as an alternative to it [53]. Tartaric acid is another bio-based acid, used for the synthesis of polyesters which can be applied in drug delivery applications as drug carriers or controlled release agents [54]. It is a chief by-product of the wine industry and can also be obtained through epoxidation and hydrolysis of maleic acid.

Bio-based polyols

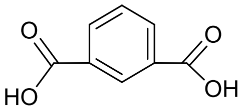
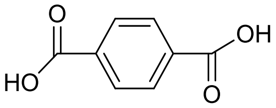
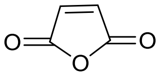
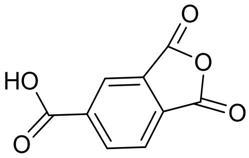
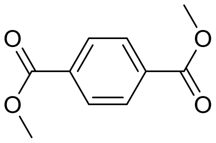
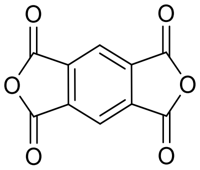
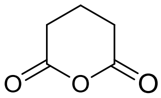
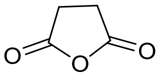
Renewable resources derived polyols are another important group of reactants in polyester synthesis (**Table 1.2**). Sugar-derived alcohols such as sorbitol, xylitol and mannitol are important polyols used for the synthesis of polyesters [55].

Table 1.2: Names, structures, and applications of a few polyols

Name	**Structure**	**Applications**
Sorbitol		Biodegradable materials
Glycerol		Biodegradable and biocompatible materials, other biomedical applications
1,3-Propane diol		Biodegradable materials
Trimethylol propane		Preparation of HPE resins
D-Mannitol		Good biodegradability, wide variety of engineering applications
Pentaerythritol		Binders for coatings, biodegradability
1,8-Octane diol		Biodegradable and biocompatible materials
Xylitol		Biomedical engineering fields such as drug delivery, tissue engineering, etc.
Erythritol		Soft biomaterials
1,4-Butane diol		Biodegradable materials
Ethylene glycol		Biodegradable
Isosorbide		Biodegradability, tissue engineering, drug delivery system, etc.

Sorbitol is a bio-based polyol obtained from D-Glucose through hydrogenation and possesses multi-functional groups lead to the formation of three-dimensional network structures. It is one of the most extracted sugars from biomass and it is a part of the “top twelve” renewable building blocks [3]. Glycerol is another important polyhydric alcohol which consists of three hydroxyl groups and took part in polycondensation reactions with dicarboxylic acids to obtain HPE. It is a by-product of biodiesel production and also a primary component of lipids. Biodegradable polyesters based on glycerol have found different biomedical applications. The bio-based product obtained from glycerol and fermentation-derived succinic acid has received industrial interest in line with the ethics of Green Chemistry [56, 57]. 1,3-Propanediol is a bio-based polyol obtained from numerous bioprocesses, and in nature, it is also achieved from glycerol by the method of bioconversion. Their polyesters showed good biodegradability [58]. Again, D-Mannitol is a component of biocompatible systems and intermediate in carbohydrate metabolism used for the synthesis of bio-based polyesters. Pentaerythritol is more photo-stable compare to glycerol due to the absence of secondary carbons in its structure, which makes it a very good candidate for binders to be utilized in exterior coatings [59]. 1,8-Octanediol is the largest aliphatic diol present in fermented foods and fruits, which is soluble in water with no reported toxicity [60]. It is commercially obtained through fermentation of glucose and used for the preparation of aliphatic polyester. These polyesters are amorphous, and T_g values are below room temperature [61, 62]. Isosorbide is another important diol used for the synthesis of aliphatic polyesters and possesses a rigid structure. It is obtained by a two step process, which include hydrogenation of D-glucose followed by dehydration of sorbitol [63]. Further, aromatic dibasic acids and different anhydrides used for the synthesis of polyester are listed in **Table 1.3**. Among them, the petro-based phthalic anhydride is a cost-effective aromatic dibasic acid and possesses advantages like UV-radiation stability, ease of handling, short reaction time, etc. [64]. Another dibasic acid is isophthalic acid which is used to make robust, fast drying and good chemical resistant coatings [65]. The oil-modified alkyd resins obtained from terephthalic and isophthalic acids was first released in a patent and exhibited better drying characteristics than the corresponding orthophthalic resins. The ester linkages formed by the reaction of carboxyl groups of terephthalic acid and hydroxyl groups of ethylene glycol results in formation of multiple poly(ethylene terephthalate) (PET) moieties in the polymer chains. This structure offers PET some advantages such as transparency, resistant to both hot and cold conditions. Polyesters are obtained from fumaric acid and maleic anhydride by carrying out the reaction in the presence of limited amounts with phthalic anhydride. They are also reported to be utilizing as monomers for development of waterborne coatings [66, 67]. Further, polyesters obtained from saturated dibasic acids and sebacic, adipic or azealic acids showed flexibility and plasticization properties.

Table 1.3: A few polybasic aromatic as well as aliphatic acids and anhydrides used for the polyester preparation

Name	**Structure**
Isophthalic acid	
Terephthalic acid	
Maleic anhydride	
Trimellitic anhydride	
Dimethyl terepthalate	
Pyromellitic anhydride	
Glutaric anhydride	
Succinic anhydride	

In literature, trimellitic anhydride and pyromellitic anhydrides are also reported for the synthesis of waterborne polyesters [68]. Oil-modified polyester resin with low viscosity is obtained using glutaric and succinic anhydrides [69].

Catalyst

In general, the polycondensation reaction of dicarboxylic acids and diols is performed inthe presence of different types of catalysts such as acid, coordinated compound, metal, etc. Literature reports the use of titanium-based catalysts like titanium (IV) isobutoxide, titanium (IV) isopropoxide, titanium (IV) *n*-butoxide, etc. for the synthesis of polyesters, but they may also increase a significant degree of degradation reactions [70, 71]. Thus, germanium and zirconium-based catalysts are developed as fascinating substitutes for these titanium-based catalysts. Further, mild polycondensation reactions are reported to be performed in the presence of triflates catalysts (e.g., lanthanide or scandium triflate) [72]. For example, scandium triflates-based catalysts have been evolved to gain bulk polycondensation of sebacic acid with the methyl ester of 1,4-Butanediol. Further, bismuth-based catalysts are also employed in aliphatic polyester synthesis [73]. Inorganic acids like H_3PO_4 or H_2SO_4 are reported to be used as a catalyst for polycondensation of sebacic acid or adipic acid with aliphatic diols under mild conditions [50]. Lewis acid catalysts like metal trifluoro methanesulfonates are used in polycondensation due to their effortless handling, low toxicity, stability and low cost [74].

Further, different catalysts such as $Ca(oct)_{2,}$ MeONa, LiOH, di-butyl tin oxide, PbO are used for alcoholysis of refined soybean oil, dehydrated castor oil and linseed oil with polyhydric alcohols like glycerol, neopentyl glycol, and pentaerythritol [75]. In addition to petroleum-based synthetic catalysts, metal catalysts, especially tin-based catalysts are not environmentally benign, thus use of enzymatic catalysts as alternatives to toxic catalysts are attractive to the users. They can be used to synthesize biodegradable as well as functionalized polyesters in the absence of solvent through highly selective processes at lower temperatures (40-90°C) compared to conventional polycondensation reactions (>150°C). A number of lipase and hydrolases obtained from *Candida antarctica* are reportedly used for the synthesis of polyesters via polycondensation or ring opening polymerization [76]. Lipase (obtained from Mucor miehei *Klebsiella oxytota*) catalysed polymerization reaction of adipic or sebacic acid with 1,4-Butanediol was performed in the presence of diisopropyl ether. They are also found to be useful for polycondensation of 1,8-Octanediol with sebacic acid in an aqueous medium. Enzyme (Lipozyme IM 60) catalyzed castor oil-based polyester resins were reported by Athawale *et al*. [77]. Some of the most widely used catalysts reported for the synthesis of waterborne polyesters are dibutyl tin dilaurate, para-toluene sulphonic acid, tin chloride, titanium (IV) *n*-butoxide, etc. [32, 10, 33, 78].

Curing agents

The thermosets of these polyesters are obtained by curing them with different types of curing agents. The combination of epoxy resins and hardeners is found to be the most widely used curing system for fabrication of polyester thermosets. The cross-linking reaction among polyester resin, epoxy resin and hardener results in a three-dimensional network structure, which converts the resin system from a viscous liquid into a hard, thermoset solid.

In general, epoxy resins are usually obtained by the base catalyzed reaction of di or polyol and epichlorohydrin or other oxirane containing reactants [79]. One of the commercial epoxy resins used in the preparation of polyester thermosets is petroleum-based diglycidyl ether-based epoxy resin [80]. However, concerned on the environment, some renewable resources derived epoxy resins like glycerol-based hyperbranched epoxy resin (HBGE), itaconic acid-based epoxy resin, vegetable oil-based epoxy resins, etc. are also used for the fabrication of polyester thermosets. In addition to epoxy, hardeners used for curing of polyesters are proton donor compounds like poly(amido amine) (PAA), anhydride, amino, phenolic, carboxylic acids, thiol, etc. which can react with epoxy resins and transform them to three-dimensional network structures under optimal processing and curing conditions [81]. Among them, amines are most widely used curing agents in epoxy matrices to develop high performing materials. Aliphatic amines like diethylene triamine, triethylene tetra-amine, hexamethylene diamine, dicyandiamide, etc. react with epoxy resins at room temperature. Cycloaliphatic amines exhibit a right balance between reactivity and final properties. Aromatic amines take longer time for curing owing to steric hindrance of the aromatic ring, but they provide excellent heat resistance, excellent mechanical properties, good electrical properties, high resistant to solvents, etc. [82, 83]. In this milieu, PAA is very useful because of its compatibility and plasticization effect.

1.3.1.2. Nanomaterials

Nanomaterials envelop a group of materials where at least one dimension is within 100 nm. They gained significant attention because they possess unique properties like magnetic, optical, electrical, etc. and these sprouting properties have significant impact in different fields such as fillers, catalysts, semiconductors, cosmetics, microelectronics, biomedical devices, etc. [84]. The incorporation of these nanomaterials in the polymeric matrix not only improves their properties but also offers some exceptional features owing to their high surface to volume ratio as well as unique physicochemical properties. The performances of these nanocomposites mainly depend on shape, specific surface area, size, aspect ratio, and uniform distribution of the nanomaterials and their compatibility with the polymer matrix [85].

Nanomaterials based on their dimensions classified into three categories: (a) zero-, (b) one-and (c) two-dimensional nanomaterials [87] (**Figure 1.2**).

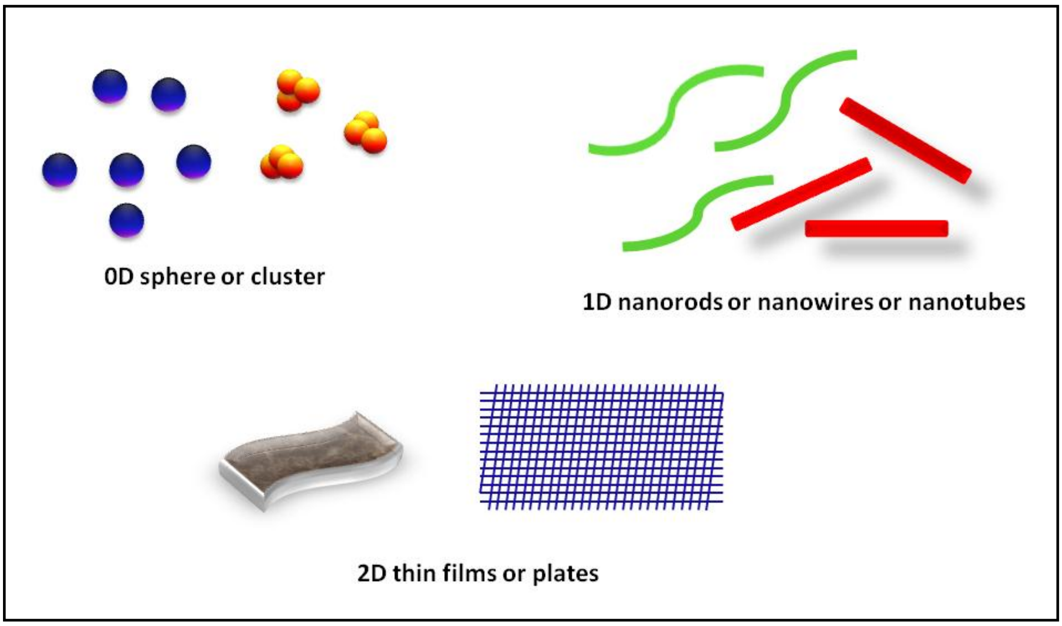


Figure 1.2: Different classes of nanomaterials

Zero dimensional nanomaterial

In this case, growth is restricted along all directions, and all the dimensions are measured within the nanoscale. They may consist of different chemical elements and also possess different shapes. They mainly include nanoparticles, nanoclusters and quantum dots [86]. Metal nanoparticles including sulfur, silver, iron, gold, copper, etc. and metal oxides nanoparticles including ZnO, TiO_2, Fe_3O_4, CuO, SnO_2, etc. are the ideal example of this class of nanoparticles [87, 88, 89, 90]. They are synthesized by various methods such as co-precipitation, wet chemical reduction, hydrothermal, microwave, sol-gel, sonochemical, reverse micelles, template synthesis, electrochemical, etc. The properties of these nanomaterials depend on the shape, size, and distribution, which can be tuned by varying the reaction parameters [91]. They are incorporated into various polymer matrices to achieve some interesting applications such as antimicrobial, electronic, catalytic, optical, photonic, sensor, etc. Further, quantum dots-based polymer nanocomposites demonstrated some unique applications such as solar cells, light emitting diodes, etc. [20].

One-dimensional nanomaterial

Materials wherein two-dimensions are in range of 1-100 nm while another dimension is in the micrometer range. This class includes nanotubes, nanowires, nanofibers, nanorods, etc. [92]. CNT are one of most exciting materials amongst them, which possesses hollow tubular structures and composed of single and multiple numbers of sp^2 hybridized graphitic carbon layers, and categorized as single-walled CNT and MWCNT respectively. They are used as the nano-reinforcing agent in different polymer matrices owing to their extraordinary properties such as electrical, mechanical, magnetic, physicochemical, etc. [93, 94]. This class also includes other nanomaterials like carbon nanofiber, cellulose nanofiber (CN), TiO_2 nanowire, etc. CN is a biopolymer which is rigid and highly crystalline due to the presence of extensive inter- or intra-molecular hydrogen bonding and hence, exhibits high strength and stiffness [95]. TiO_2 nanowire is the most widely used nanomaterial in the fields of photocatalysis and solar energy conversion because of its attractive characteristics like non-toxicity, good photoactivity, easily accessible, chemical durability, etc. [96].

Two-dimensional nanomaterial

In this class of nanomaterials, one dimension is in the nm range while other two dimensions are not restricted to the nanoscale. This class consists of nanofilms, nanolayers, etc. of graphene, GO, reduced GO (RGO), clay, etc. [97]. Nanoclays are silicates layers and depending on the type of clay; individual layers could be arranged either $[SiO_4]^{4-}$ tetrahedrally or $[AlO_3(OH)_3]^6$ octahedrally. The aluminosilicate layers arrange themselves over one another through van der Waals forces and gap between the layers is called ‘interlayer’ spacing [98].

Among all these nanomaterials, GO as a two dimensional and CD as a zero-dimensional nanomaterial have been found most suitable for waterborne polymers especially polyester nanocomposites and hence are elaborated here.

GO

Graphene is one of the smartest two-dimensional carbon nanomaterials which have attracted remarkable interest over the past three decades owing to its unique two-dimensional structure, huge surface area, aspect ratio, Young’s modulus, outstanding thermal, electrical, mechanical and catalytic properties, etc. [86]. It consists of a single-atom-thick planar sheet consist of a sp^2 -bonded carbon structure where carbon atoms are arranged in a honeycomb manner. Each atom consists of four bonds, three σ bonds and one π-bond with three neighboring atoms in the plane and a carbon atom out of the plane respectively [99]. But graphene is difficult to incorporate in polymer matrices, especially in waterborne polyesters. In this milieu, GO comprises a single layer of graphite oxide, which is generally produced by oxidation of graphite and subsequent dispersion and exfoliation by water molecules [100]. It possesses great varieties of oxygeneous functional moieties which are mostly present in the form of epoxy and hydroxyl groups on the basal plane, carboxylic, carbonyl, lactone, phenol and quinone at the edges of the graphene sheet. The most charming property of GO is that modifiable surface properties can be achieved from the oxygeneous functional groups present therewith [101]. It is found to be a good nano-reinforcing agent in different polymer matrices owing to its unique and fascinating properties for a variety of applications such as hydrogen storage, supercapacitors, sensors, batteries, transparent conductive films, solar cells, photocatalyst, etc. [102].

CD

CD is the rising star of zero-dimensional carbon nanomaterials in the field of material science. It is a good alternative to traditional semiconducting quantum dots. It contains carbon, oxygen, and hydrogen decorated with various functional groups on the surface with less than 10 nm in size [103]. The structure has sp^2 and sp^3 hybridized carbon atoms, numerous surface functional groups and possesses favorable attributes like aqueous solubility, low toxicity, size and wavelength dependent PL properties, photostability, functionalizability, use of cheap and abundant raw materials, etc. It is found applications in different fields like bio-imaging, sensing, gene or drug delivery, catalysis, etc. owing to its unique properties [104].

CD-based nanohybrid

Nanohybrids are composed of two or more different nanomaterials linked together by covalent and non-covalent bonds. They have attracted significant attention as their use affords a chance to generate an enormous number of new advanced materials with multifaceted applications through combinations of their distinct properties. The unique properties of nanohybrid can be beneficial to numerous fields such as catalysis, optical, biomaterials, electronics, sensing, coating, energy storage, etc. [105]. In general, nanohybrids can be obtained by decorating zero-dimensional nanomaterials on the surface of one or two- dimensional nanomaterials and are used for multifaceted applications [104]. CD-based nanohybrid using different zero-dimensional nanomaterials such as Au, Pt, Pd, Cu_2O, ZnO, Fe_2O_3, TiO_2, NiFe, RuO_2, etc. are reported for different advanced applications like photo-catalysis, sensors, solar cells, energy storages, supercapacitors, etc. [106-109]. Metal oxide nanoparticles are already reported in different fields such as photo-catalysis, electrocatalysis, energy storage, etc. while CD also possesses some unique features, as mentioned earlier. However, to combine their properties and performances, suitable nanohybrids of them have been developed through different synthetic approaches.

1.3.2. Methods

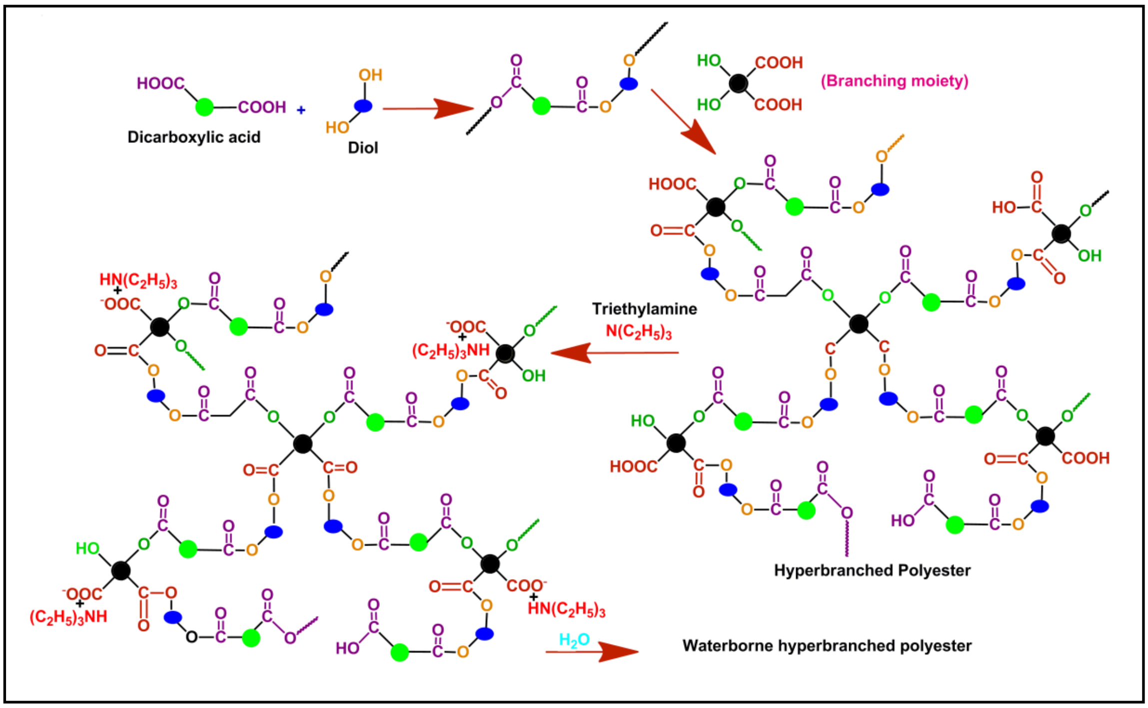
Preparative methods of polyester, GO, CD, CD-based nanohybrids, and polyester nanocomposites are discussed in this section.

1.3.2.1. Preparative method of polyester

Most commonly, polyester is synthesized by the step-growth polymerization of diols with diacids. This reaction can take place in the presence of an external catalyst. However, the acid monomer can also act as a self-catalyst. However, this approach involves the removal of water as the by-product that needs relatively high temperature and makes the process energy-intensive [110]. Further, aliphatic polyesters are generally obtained through the chain-growth ring-opening polymerization process of lactones of AB-type monomers [111]. However, HPEs conventionally, are produced by the polycondensation of either mutually reactive multifunctional monomers, A_x and B_y (where x and y ≥2) through $A_x + B_y$ strategy or AB_x monomers [112]. Further, polymers obtained from AB_x monomers have barely one probable composition from each monomer. A general scheme for the synthesis of HPE and WHPE is shown in **Scheme 1.1**.

In this context, abundant literature is found for the synthesis of bio-based linear and hyperbranched as well as waterborne polyesters through different approaches. Kolanthai *et al.* [113] reported the synthesis of soybean oil-based polyesters by melt condensation of sebacic acid and epoxidized soybean oil polyol with citric acid. A series of bio-based polyesters obtained from glycerol, itaconic acid and diols through melt polycondensation was reported by Dai *et al.* [10]. Similarly, linear aliphatic polyesters were obtained from bio-based monomers like 1,10-Decanediol, sorbitol, and dimethyl adipate through polycondensation reactions in the presence of 'SPRIN liposorb' as the catalyst [3]. Furan containing bio-based polyesters was synthesized by polycondensation of 2,5-bis hydroxymethyl fumaric acid with different diacid ethyl esters such as bio-based diethyl succinate, diethyl suberate, diethyl glutarate, diethyl sebacate, diethyl adipate and diethyl dodecanedioate diacid-ethyl-esters using *Candida antarctica* Lipase

B enzyme catalyst. [9]. Synthesis of elastic polyesters was reported by Djordjevic *et al*. by performing the esterification reaction among 1,8-Octanediol, citric acid and sebacic acid in the absence of catalyst [48]. Sathiskumar and Madras [114] synthesized biodegradable polyesters by carrying out the melt polycondensation of two different diacids (sebacic acid and citric acid) and castor oil with D-Mannitol in the absence of catalyst.



Scheme 1.1: Scheme for synthesis of HPE and WHPE

Further, Kambouris and Hawker prepared a fully or partly aliphatic HPEs by polycondensation of methyl-4, 4-bis(4´-hydroxyphenyl) pentanoate using cobalt acetate catalyst. Similarly, partially aliphatic HPE was reported by Turner *et al*. through melt polymerization of 5-(2-hydroxyethoxy)-1,3-benzenedicarboxylic acid using dibutyl tin diacetate as a catalyst. Again, the synthesis of aliphatic HPE by acid catalyzed esterification of bis-MPA and 2-ethyl-2-(hydroxymethyl)-l,3-propanediol (core molecule) was reported [115]. Stefani *et al.* [116] synthesized three different HPE by performing the reaction between α,ω-dicarboxylic acid and triglycerol in a 1:1 molar ratio at 160 °C in the presence of $Ti(OBu)_4$ catalyst. Further, synthesis of HPEs was reported by Zhang *et al.* [117] through $A_2 + B_3$ step-growth polymerization of an equimolar amount of glycerol and adipic acid in the presence of dibutyltin oxide. HPE of first, second, and third generations were synthesized by performing the reaction of AB_2-

type monomer (bis MPA) with core moiety (pentaerythritol, glycerol or trimethylol propane) [30]. Saeed *et al.* [118] synthesized aromatic-aliphatic moieties containing hydroxyl-terminated HPE through A_2+B_4 melt polycondensation of pentaerythritol and isophthalic acid. Linear and terminal phenol groups terminated HPE copolymers were prepared by reacting B_3 monomer (phloroglucinol) with different feed ratios of adipoyl and terephthaloyl chloride (as the A_2 monomers) through one-pot $A_2 + B_3$ polycondensation strategy [119]. Stumbe and Bruchmann [29] reported the synthesis of HPE through $A_2 + B_3$ polycondensation reaction of glycerol and adipic acid in the absence of solvents and the presence of tin catalyst. Du *et al.* [120] synthesized fully bio-based HPE by performing step-growth polymerization of glycerol and adipic acid or succinic acid at 150°C in toluene through the A_2 + B_3 approach. In this case, glycerol acts as a branch generating moiety.

In addition, many reports are also available in the literature on synthesis of waterborne polyesters. These polyester are generally terminated either by carboxylic or hydroxyl groups. In order to achieve good dispersion stability, polyester should contain a comparatively large amount of carboxylic groups. Further, for complete ionization of these carboxylic groups, excess volatile amine (triethyl amine) or strong base should be used [121]. Hydroxyl functionalized water-soluble HPE was synthesized using phthalic anhydride, pentaerythritol, pyromellitic dianhydride and 1,1,1-tris(hydroxymethyl) propane. For this purpose, polyol was first synthesized by performing the reaction between pentaerythritol and pyromellitic dianhydride at 200 °C using para-toluene sulphonic acid as the catalyst and dimethyl formamide as the solvent. Subsequently, this polyol was reacted with phthalic anhydride in the presence of the same catalyst and xylene at 140°C, resulted in carboxyl functionalized HPE [122]. Synthesis of castor oil-based waterborne alkyd in the presence of environmentally friendly solvent was reported by Pathan and Ahmad [78]. Further, this alkyd was cured of butylated melamine formaldehyde [78]. WHPE composed of a multi-hydroxyl functional aliphatic polyester end-capped core with salt-like groups and an epoxy (oxirane) group of CARDURA E10 was also reported. Asif and Shi [32] reported waterborne hyperbranched aliphatic HPE with Boltorne H20 polyester polyol core. The carboxylic groups were end-capped by methacrylic groups and salt like in four different ratios, i.e. 10:6, 8:8, 6:10 and 4:12. The end-capped carboxylic groups containing HPE was mixed with p-hydroxy anisole and *N*, *N*-dimethyl benzylamine. Further, salt-like structures and methacrylate groups were introduced into chain ends of waterborne polyester by adding glycidyl methacrylate to the reaction mixture and the reaction was carried out at 70°C for 8 h followed by neutralization of the remaining carboxylic groups with triethylamine [32]. On the other hand, bio-based water-soluble polyesters were obtained by the bulk polycondensation of maleic anhydride, isosorbide, and poly(ethylene glycol) using titanium(IV) *n*-butoxide catalyst. Water-soluble polyesters were also synthesized by using the long aliphatic chain of 12, 18 and 22 carbon atoms mono-l-alkyl citrates [123]. Further, water-soluble HPE was synthesized by using pentaerythritol and trimethylolpropane as branching center and trimellitic anhydride as waterborne functional groups. The polyester was neutralized with trimethylamine at 80 °C to obtain the water solubility [124].

Further, in literature patents are also available on preparative methods of hyperbranched and waterborne polyester [125-131]. Nakae *et al.* [130] invented paint of waterborne polyester for electrodeposition and the top coat of automobile bodies.

1.3.2.2 Preparative method of graphene

The first report on graphene appeared in 2004 which was obtained by mechanical exfoliation of graphite [132]. Single and few-layer nanosheets of graphene were first achieved through Scotch-tape method by mechanically exfoliating of graphite layers and by chemical vapor deposition [133]. The other approach to obtain graphene sheets is solvent stripping method which destroys van der Waals force between the graphite layers in a solvent [134]. Redox method is another popular method to prepare graphene and graphite oxides where graphite crystal was treated with strong oxidizing agents and oxygen-containing functional groups are generated on the sheet [135]. A practical approach for bulk-scale production of graphene materials is the chemical route. The chemical method used for the synthesis GO and graphite oxide are the same, but these two are different in their structures [136]. Graphite oxide is a group of layers GO, and exfoliation of graphite oxide produces GO which is single layer sheet of graphite oxide. There are many methods like mechanical to exfoliate graphite oxide to GO, but one of the most common methods is the sonication of graphite oxide in water or organic media [137]. GO was first obtained by addition of potassium chlorate to the slurry of graphite in fuming HNO_3, which was reported by Brodie [138] in 1859. Later, Staudenmaier [139] has slightly improved this procedure by using concentrated HNO_3 as well as H_2SO_4 to enhance the acidity of the mixture and by adding the chlorate in several aliquots during the reaction. The little change in this method provided highly oxidized graphite oxide and simplified the synthesis process of GO. Hofmann *et al*. [140] prepared graphite oxide in 1937 by oxidizing graphite using concentrated sulfuric acid and nitric acid as well as $KClO_3$. Hummers [141] in 1958 reported a simple method for synthesis of GO from graphite by oxidizing with $NaNO_3$ and $KMnO_4$ in concentrated H_2SO_4, which is the most commonly used method in recent times. Tour’s group [142] modified Hummer’s method by using H_2SO_4, H_3PO_4 and double amount of $KMnO_4$ to replace $NaNO_3$ as the use of $NaNO_3$ emits toxic gasses. This approach enhances the efficacy of oxidation of graphite to graphite oxide and also gives a larger quantity of graphite oxide relative to Hummers' method. Further, it prevented the evolution of toxic gases like NO_2 and N_2O_4. However, the fast and efficient route for the large-scale fabrication of graphite oxide is oxidation of graphite using benzoyl peroxide [143]. Furthermore, another oxidizing agent like Jone’s reagent (H_2CrO_4/H_2SO_4) was used for the preparation of GO [136]. In 2013, Sun and Fugetsu [144] established a direct technique to generate GO using expanded graphite as the carbon precursor. The intercalation of $KMnO_4$ between graphitic layers formed impulsive expansion which appears like the foam of graphitic material, and the reaction occurs in the presence of sulfuric acid. This method is considered as a better procedure as the ratio of graphite: H_2SO_4 was reduced to 1:20 and extra reagents were eliminated. Another preferred method to produce GO was proposed by Peng and co-workers [145] in 2015, which uses a strong oxidant (K_2FeO_4). Here, a mixture of graphitic flakes and K_2FeO_4 dispersed in concentrated H_2SO_4, were loaded into a reactor and stirred at room temperature for 1h. The final product was washed with water repeatedly followed by centrifugation to acquire highly water-soluble GO. **Figure 1.3** represents the various methods used to obtain GO.

1.3.2.3. Preparative method of CD

Fluorescent CD with size 1 nm first appeared in 2004 accidently during purification of single-walled carbon nanotubes which was fabricated by the arc-discharge method as reported by Xu *et al*. [146]. CD are usually synthesized by following two synthetic approaches – ‘top-down’ and ‘bottom-up’ (**Figure 1.4**) [147].

Top-down approaches

In these approaches, CD are formed from larger carbon structures like activated carbon, CNT, nano-diamond, carbon soot, graphite and graphite oxide by different methods such arc discharge, electrochemical oxidation and laser ablation [148]. A brief overview of these methods is given below.

Arc discharge

First CD was achieved by this method when the black suspension obtained after oxidation of soot with nitric acid was subjected to gel electrophoresis. This method is used to prepare CD from the soot of crude CNT by oxidizing 3.3M HNO_3 and then extracting them with an alkaline solution. Further, these materials are purified by gel electrophoresis to get the final product [146].

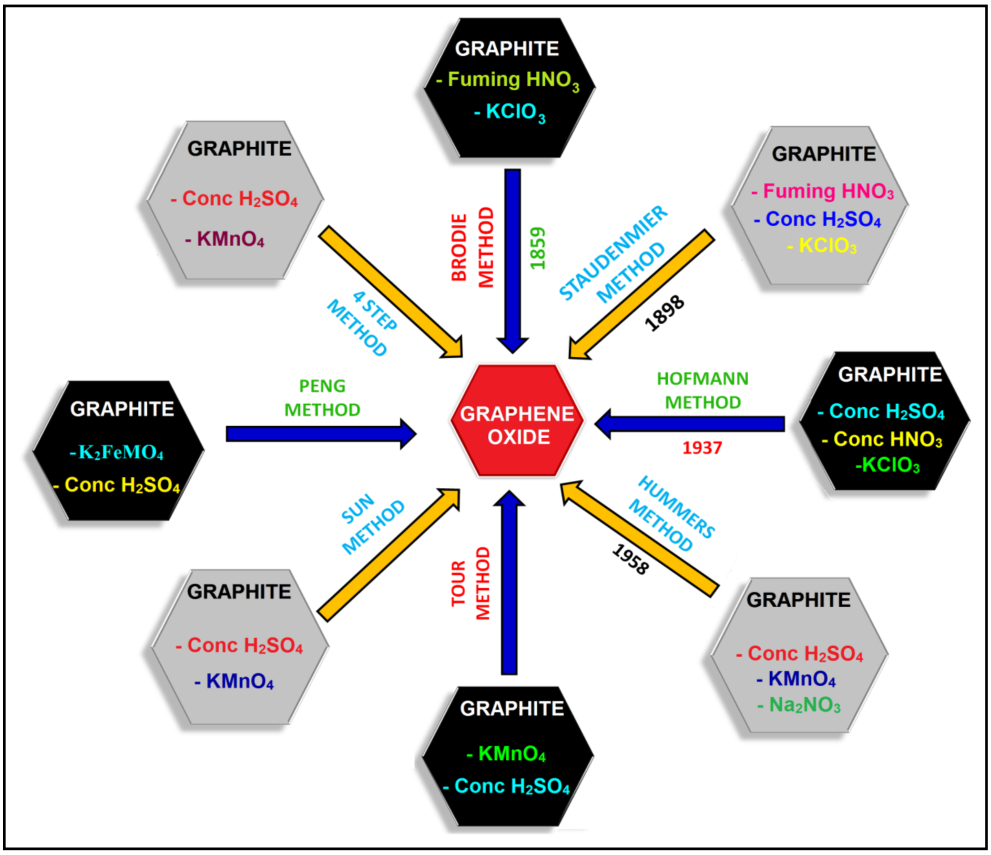


Figure 1.3: Different approaches for the preparation of GO

Laser ablation

It is one of the eco-friendly, facile and effective methods for preparation of CD which can tune surface states of particles [149]. Li *et al*. [150] reported the preparation of CD by laser ablation method from a carbon target in the presence of water vapor and a carrier gas (argon) under 75 kPa and 900°C. After refluxing with HNO_3 for 12 h followed by passivation of surface by PEG1500N or poly(propionyl ethyleneimine-co-ethyleneimine) led to the formation of CD with bright luminescence. Similar fluorescent CD was also reported by Hu *et al*. [151] which were obtained by laser irradiation of a carbon suspension in the presence of organic solvent. In literature, many reports are available on the synthesis of CD by this technique. However, this method possesses some demerits including low quantum yield (QY), poor control over the size and high energy consumption.

Electrochemical oxidation

In this method, different precursors such as large carbon materials like graphite, carbon fiber, graphene, etc. are used for the preparation of CD. CD from these precursors can be obtained by using three different electrodes: a working electrode (graphite), a counter electrode and the reference electrode (Ag/AgCl) in different aqueous electrolytes like phosphate buffer, NaH_2PO_4, 1-butyl-3-methylimidazolium tetrafluoroborate [152, 153]. Zhou *et al*. [154] reported the first electrochemical process to prepare CD by growing CNT on carbon paper cell and by inserting them into an electrochemical cell containing degassed acetonitrile and 0.1M tetrabutyl ammonium perchlorate. Ming *et al*. [155] later prepared CD using graphite through one step electrochemical approach in order to increase the scale of production and minimize the cost of starting material. The advantages are low cost, ease of process, prospective for mass production, and abundance of raw materials, while avoiding the use of toxic or harsh chemicals. However, the main drawback of this process is the purification of synthesized particles. A few important methods for obtaining CD are summarized in **Figure 1.4.**

Bottom up approach

This approach requires external energy such as microwave pyrolysis, ultrasonication, and heating to prepare CD from some small molecules such as fructose, glucose, etc. The brief discussions of these methods are given below.

Microwave

One of the low cost and rapid methods for preparation of CD is microwave irradiation of organic precursors. Green luminescent CD was obtained by one minute microwave irradiation of sucrose and diethylene glycol [156]. Polyethylenimine functionalized CD was reported by Liu *et al*. [157] through microwave heating of glycerol and branched PEI-25k mixture at 700 W. Another fluorescent CD was reported by Mitra *et al*. [158] which achieved through microwave irradiation (55-60s) of poly(ethylene glycol) 200 and poly(vinyl alcohol) in the presence of ortho-phosphoric acid. Many reports are available on the synthesis of CD by this method. However, disadvantage related to this method is control over the size of the obtained particles.

Pyrolysis

One of the methods to obtain CD with tunable and uniform sizes is the pyrolysis of an organic precursor in nano-reactors. Porous silicas are the most commonly used nano-reactors owing to their thermal stability, tunable and easily acquired textures and easy removal. The method involves three steps: absorption of organic components into nano-reactors through capillary force, pyrolysis of the organic components into the carbonaceous matter, the release of as-prepared CD by removing the nano-reactors. CD obtained by pyrolysis of different natural products such as coffee, flour, eggshell membrane, green tea, amino acid, pomelo peel, tobacco, etc. are reported in the literature [159-163].

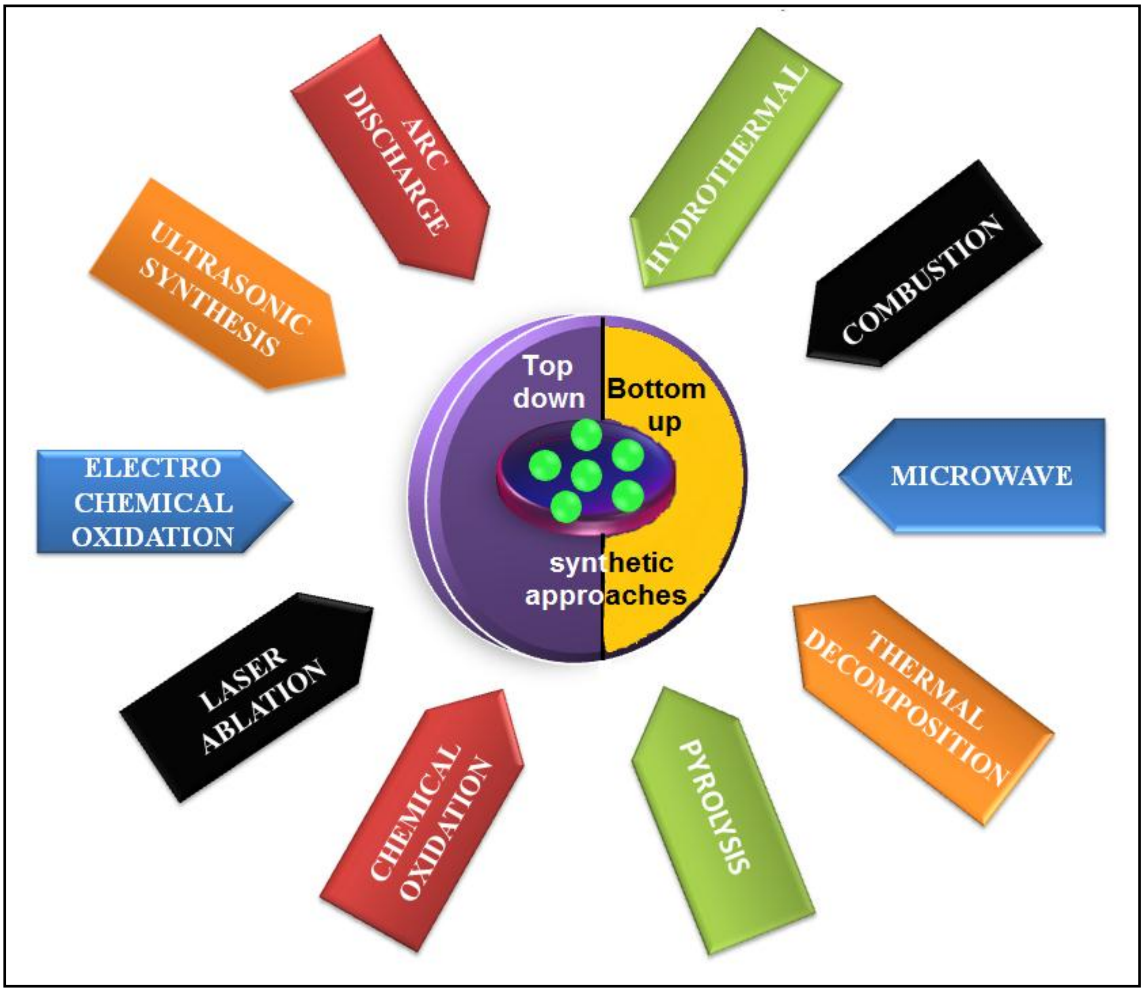


Figure 1.4: Different preparative routes for CDs

Hydrothermal/Solvothermal

It is a low cost, facile and environmentally friendly one-pot method for the preparation of water-soluble CD from various raw materials. It involves carbonization of small organic molecules in the presence of water/organic medium under high pressure and temperature [164, 165]. In literature, lots of reports are available for production of CD by this route.

Sahu *et al*. [166] obtained a highly fluorescent CD (QY 26%) from orange juice through one step hydrothermal treatment and applied in bio-imaging owing to their high photostability. The amino-functionalized fluorescent CD was prepared by hydrothermal carbonization of chitosan at 180°C for 12 h and can be used directly as a novel bio-imaging agent [167]. CD is also prepared by hydrothermal treatment of different bio-based precursors like citric acid, banana juice, glucose, chitosan, protein, egg white, garlic, sweet pepper, green tea, coffee ground, etc. find applications in different fields including bio-imaging, bio-sensing, bio-imaging, photo-catalysis, drug delivery, etc. [168].

1.3.2.4 Preparative method of CD-based nanohybrid

Different preparative routes are reported for fabrication of CD-based nanohybrids which included a solvothermal/hydrothermal method (*in-situ*), physical mixing, chemical reduction, and *ex-situ* techniques.

In physical mixing technique, the nanohybrids are obtained by mixing a CD solution with the dispersion of metal nanoparticles by mechanical shearing force followed by ultrasonication. Different kinds of nanohybrids like CD/Au, CD/ZnO, CD/TiO_2, CD/Cu_2O, etc. are prepared by this method. These nanohybrids are used for different applications such as photocatalysis, energy storage, catalysis, etc. [169-172]. However, one of the disadvantages related to this method is the poor interaction between CD and metal nanoparticles. Thus, researchers developed chemical reduction and hydrothermal method for the preparation of different types of CD-based nanohybrids.

In chemical reduction technique, CD acts as a reducing agent owing to its polar functional groups including hydroxyl, carboxylic acid, carbonyl, and epoxy. These groups can reduce the metal ions by transferring electrons, and the primary benefit of this technique is that CD can also act as a stabilizing agent owing to the presence of these oxygeneous polar functional groups on their surface. Thus, the growth of metal nanoparticles in most of the cases begins on the surface of CD to form the nanohybrid. Different metal-based nanohybrids like CD/Pt, CD/Cu_2O, CD/Au, CD/Ag, etc. were prepared by this method and used in different fields like sensors, solar cell, optoelectronics, catalysis, etc. [106-109].

At present, hydrothermal is a simple, facile and most widely used one-pot preparative route to obtain CD-based nanohybrid. In this case, precursors of CD were mixed with an aqueous solution of the metals salts before carrying out the hydrothermal process. It is mostly used to create strong interactions between CD and metal nanoparticles as well as to achieve controlled shape and size of the nanohybrids. Different kinds of nanohybrids like CD/TiO_2, CD/Fe_2O_3, CD/ZnO, CD/Au, CD/Fe_3O_4, CD/g-C_3N_4, etc. were obtained by this method. These nanohybrids found applications in different fields such as photo-catalysis, sensors, supercapacitors, solar cells, electrocatalyst, sodium and lithium ion batteries, etc. [173-178]. **Table 1.4** represents different CD-based nanohybrids with their preparative methods and applications.

1.3.2.5. Preparative methods of polyester nanocomposites

Nature always constructs smart materials with extraordinary properties and functions by combining organic and inorganic components at the nanoscale. Looking to nature, scientists in the field of materials developed a new synthetic strategy to produce materials called nanocomposites. Different methods like the solution, *in-situ* polymerization and melt-mixing are developed for the fabrication of nanocomposite with the polymer. A brief overview of various fabrication methods of polymer nanocomposites is discussed below.

Solution technique

In this technique, the appropriate solvent is required, which swell and disperses the nanomaterials. The dispersed nanoparticles are incorporated into polymer matrix using mechanical and ultrasonic shearing forces, followed by precipitation or evaporation of solvent resulted in the nanocomposites. Both exfoliated and intercalated nanocomposites are produced based on the degree of mixing. The total entropy of the process decreases owing to the detention of the chains, which is again remunerated by desorption of solvent molecules and resulted in intercalated nanocomposite [190, 81]. This method can be attractive for water soluble polymers, if water could be used in place of organic solvents. Various types of polyester nanocomposites were fabricated by use of this technique. The nanocomposite of polyester and MWCNT was fabricated by this approach [191]. Sirohi *et al.* [192] further applied this method to fabricate ZnO-based polyester nanocomposite. However, this technique possesses some disadvantages like high cost, use and removal of organic solvent which is environmentally and industrially not acceptable.

In-situ technique

This technique is developed to create better interaction between polymer matrices and the nanomaterials. Further, it minimizes or eliminates the use of solvent and reduces the energy necessary for the mixing process. In this technique, first nanomaterials are dispersed or swollen in a liquid monomer or pre-polymer and then polymerized using an initiator or catalyst.

Table 1.4: Methods of preparation and applications of different types of CD-based nanohybrid

Nanohybrid	**Method of preparation**	**Applications**	**Reference**
	Hydrothermal followed by ion exchange and calcinations	Sodium and lithium ion Batteries	[179]
CD/TiO_2	Sol-gel auto-combustion	Photocatalyst	[180]
	Electrospinning	Photocatalyst	[181]
	Hydrothermal	Photocatalyst	[173]
Core shell CD/silica	Sol-gel	LED plant grow light	[182]
N-doped CD/Pt	Chemical reduction	Methanol electroxidation	[106]
CD/ZnO	Hydrothermal	Photocatalyst for degradation of toxic gases (benzene and methanol)	[176]
	Sol-gel	Photocatalytic degradation of Rhodamine B (RhB)	[183]
	Physical mixing	Photocatalyst	[170]
CD/Cu_2O	Ultrasonic method	Photocatalytic degradation of dye	[184]
	Chemical reduction	Photocatalyst	[107]
	Hydrothermal	Photocatalytic degradation of methanol and benzene	[185]
CD/Fe_2O_3	Solvothermal	Photocatalyst	[174]
CD/Au	Hydrothermal	Fluorescent detection of mercury	[175]
	Chemical reduction	Solar cell	[108]
	Physical mixing	Sensor	[169]
CD/Fe_3O_4	Ultrasonic treatment	Energy storage	[186]
	Solvothermal	Photocatalyst	[177]
	Hydrothermal	Photocatalytic H_2 evolution	[178]
CD/g-C_3N_4	Pyrolysis	Water splitting	[187]

CD/Bi$_2$WO$_6$	Hydrothermal	Photocatalyst	[188]
	Chemical reduction	Sensors	[109]
CD/Ag	Chemical reduction	Solar cell	[189]

The low viscosity of the monomers replicates the necessity of low energy for the mixing process. Stable polymer nanocomposites are formed by the presence of different secondary interactions. In case of resin, the nanomaterials not only assist in cross-linking reaction but may also influence the polymerization process. It is the most favorable method for attaining exfoliated structure in polymer/clay or layer silicate-based nanocomposites [193].

Melt-mixing technique

In this technique, the polymer is heated above its softening temperature and mixed with the nanomaterials under a shearing force. Mixing can be done using screw intender, mixer, injection molding, rollers, etc. In this process, there is entropy loss related to the confinement of a polymer melt by the formation of nanocomposite and entropy gain is related with the layer separation. This method may not be as efficient as that of the solution, and *in-situ* technique and but can apply to produce nanocomposite using traditional polymer processing techniques like extrusion and injection molding in polymer processing industry [81, 190, 194].

In addition, some other techniques like sol-gel process, template synthesis, ball milling, plasma-induced polymerization, thermal spraying process, etc. are reported in the literature for fabrication of nanocomposites [81]. However, practical applicability of these techniques is hindered in many cases due to the high cost and poor dispersion of nanomaterials in the polymer matrix.

In literature, different types of polyester nanocomposite using a variety of nanomaterials are reported some of which are enlisted with their salient features in **Table 1.5**. Konwar and Karak [11] reported clay-based polyester nanocomposite by mixing the dispersed clay in xylene with acrylate-modified polyester resin with the help of mechanical stirring and ultrasonication. Then, methyl ethyl ketone peroxide and cobalt-octoate are incorporated in the above mixture. The same group reported highly branched water dispersible polyester nanocomposite using different wt% of hydrophilic bentonite nanoclay [195].

Table 1.5: Polyester nanocomposites, their preparative method and salient features

Nanocomposite	**Preparative method**	**Salient feature**	**Reference**
Aromatic polyester/ CNT nanocomposite	Melt blending	Improved mechanical properties	[198]
Polyester/exfoliated graphite nanocomposite	Melt pyrolysis	Improved tensile stiffness and dimensional stability	[37]
Unsaturated polyester/nano-cellulose nanocomposite	Mechanical mixing	Favorable rheological behavior	[199]
HPE/ZnS nanocomposite	Free radical polymerization	Interesting optical properties including good transmittance	[12]
Waterborne polyester/ clay nanocomposites	Solution method	Intercalated chemistry focused	[200]
Polyester/clay nanocomposite	Solution technique	Enhanced mechanical, thermal and biodegradability	[11]
Branched polyester /clay nanocomposite	*Ex situ*	Improved mechanical, thermal and biodegradability	[195]
Polyester/ZnO nanocomposites	Ball mixing	Provided anti-corrosion behavior	[201]
HPE/TiO_2 nanocomposite	*Ex-situ* and *in-situ* method	Provided photocatalytic activity	[14]
Polyester/ Ag Nanocomposite	Sol-gel method	Provided antistatic and antibacterial activities	[202]
Branched water dispersible polyester/ clay nanocomposite	*Ex situ*	Improved biodegradability and mechanical properties	[197]
Polyester/GO nanocomposite	*Ex situ*	Enhanced mechanical and thermal properties	[19]
Polyester/SiO_2	Ultrasonication	Enhanced modulus,	[196]

Nanocomposite	permeability, thermal stability

The nanocomposites showed enhancement in mechanical, thermal and chemical properties as well as biodegradability behavior. Similarly, SiO_2-based polyester nanocomposites were fabricated by ultrasonic irradiation process. In this case, γ-glycidyloxypropyl trimethoxysilane was used as the coupling agent, which may enhance the compatibility between the polyester and silica [196]. Chen *et al*. [197] also fabricated silica- based polyester nanocomposite by both *in-situ* polymerization and blending methods. Sirohi *et al*. [192] fabricated polyester nanocomposite by using different wt% of ZnO nanoparticles. The nanocomposite showed considerable enhancement in thermal stability, antimicrobial behavior and UV protection as well as retaining the biodegradability of the material. Bora *et al*. [19] fabricated polyester nanocomposites by dispersing GO in tetrahydrofuran by ultrasonication and mixing with polyester resin using mechanical shearing force and ultrasonication. Further, methyl ethyl ketone peroxide hardener was added into the reaction mixture and subsequently cured to obtain the desired thermosetting nanocomposite. Again, ZnS-based polyester nanocomposite was reported by Zhao *et al*. [12].

1.4. Characterization

Different types of techniques are necessary to realize physicochemical features of polyester, GO, CD and polyester nanocomposites, which are highlighted in this section. Furthermore, different testing methods used for evaluation of their properties are also highlighted herein.

1.4.1. Analytical techniques

In order to understand the physical properties of polyesters, the determination of acid value, saponification value, hydroxyl value, viscosity, molecular mass, etc. are important. The acid value is calculated following the standard ASTM D 974 method, and low value confirms the presence of less free acids in the polyesters. Further, lowering of acid value with the reaction time authenticate the reaction between the polyol and the polybasic acid. The extent of reaction in the synthesis of polyesters is monitored by determining the acid value at different time intervals of the esterification reaction [203, 204]. Similarly, hydroxyl value provided the hydroxyl content and defined as the numbers of milligram of KOH equivalent to the hydroxyl content of one gram of the polyester. The value is determined by refluxing polyester resin with excess amount of maleic anhydride solution using triethyl amine as the catalyst. The excess free acid is back titrated with the standard KOH solution using phenolphthalein as an indicator [205]. Further, saponification value is determined by following ASTM D 1962 method indicates the average molecular weight and chain length depending on the amount of basic solution required to neutralize the carboxylic groups present per unit gram of the resin [204]. The specific gravity of the resins is based on Archimedes principle and calculated as per the standard ASTM D792 method using a standard specific gravity bottle [19].

Further, the calculation of solution viscosity is also important in order to gaining the information regarding the frictional property and chain dimensions of HPE which is measured with the help of a capillary viscometer like Ubbelohde viscometer. Furthermore, molecular weights of polymers are generally determined as the average values as they are composed of different chain lengths. Gel permeation chromatography (GPC) is a rapid, accurate and convenient technique to determine weight average molecular weight (M_w) and polydispersity index (PDI) of polyesters, wherein the polymer molecules are separated according to their size and identified from their action towards refractive index or UV absorption [81, 206].

1.4.2. Spectroscopic techniques

Fourier transforms infrared spectroscopy (FTIR)

It is an important technique used for preliminary characterization of materials which provides information about the presence of various functional groups in them. Presence of carbonyl and hydroxyl groups of polyesters is established by the existence of the stretching bands at around 1750 and 3400 cm^{-1} respectively in their FTIR spectra [113]. Further, different characteristic bands at 1060, 1250, 1365, 1720, 3450 and 1620 cm^{-1} in the FTIR spectrum of GO established the presence of C–O, C–O–C, C–OH, -O-H and -C=O groups respectively. The appearance of oxygen-containing functional groups further confirmed the oxidation of graphite to GO [100]. FTIR spectrum of CD not only provides the information about the presence of different functional groups like hydroxyl, epoxy, carbonyl, etc. but also gives an idea to scrutinize the doping of heteroatoms in CD [166]. The presence of phosphates (P=O and P-OR), organosiloxane (Si-O-Si/ Si-O-C), alkyl sulfide (C-S), amide/amine (-CN/NH_2), etc. in CD indicates the introduction of phosphorus, silicon, sulfur, nitrogen, etc. [207, 208]. Further, it also predicts the nature of functional groups, the presence of different types of chemical and physical interactions of nanomaterials with the polymer matrix. The stretching bands of different functional groups of a nanomaterial are shifted to higher or lower values, or the percent of transmittance values are diminished due to these interactions [19].

Nuclear magnetic resonance spectroscopy (NMR)

It is one of the imperative techniques used for structural characterization of the polymer. ^1H NMR and ^{13}C NMR spectral analyses authenticate the presence of different kinds of protons and carbons in different chemical environments [209]. Further, the details scrutinize of the spectrum help to calculate the degree of branching (DB) and confirmed the hyperbranched structure of polyester. According to Frechet’s equation, DB is considered as the ratio of the sum of the integration value of dendritic (D) and terminal (T) units to the sum of the integration value of D, linear (L) and T units [210]. Zagar and Zigon [43] calculated the DB of bis-MPA-based aliphatic polyester by the use of the above formula and established the hyperbranched structure. Further, this technique is also applied to gain further structural insight into CD by identifying the surface functionality of CD, to determine the element states (e.g., C, N, and P) in CD, and to examine the nature of their bonding onto the particle surface [211].

UV-visible spectroscopy

It is generally used to characterize nanomaterials particularly GO, CD, metal oxide nanoparticles and also polyester [212, 99]. The appearance of particular absorbance peaks in the UV-visible spectra is due to π-π^* and n-π^* transitions of functional groups present in polyesters and nanomaterials [99]. However, nature, position and intensity of the peaks emerge differently with different doses of nanomaterials in polymer nanocomposites [20]. Further, the band gap of nanomaterials as well as nanocomposites can also be determined from the absorbance values [156]. This tool is also used to measure the optical transparency of polyester thermosets and their nanocomposites. The percent of transmittance of visible light by the thermosets is measured using absorbance in the visible range.

PL spectroscopy

One of the important tools to evaluate the optical properties of nanomaterials like CD is PL spectroscopy. CDs are active in the UV-vis region of the electromagnetic spectrum, and the fluorescent emission of them shows λ_{ex}-dependent behavior [103]. Further, PL spectroscopy together with UV-vis spectroscopy can be used to determine the QY of CD. The yield is determined by a relative method using quinine sulfate with known QY as the reference. Basically, PL spectra of solutions of CD and quinine sulfate with the same UV absorbance at the identical λ_{ex} are recorded and the simple ratio of integrated PL intensity of the two solutions will give QY of CD [103].

Raman spectroscopy

It is an important technique and extensively used for the characterization of carbon-based nanomaterials like CD, GO, RGO, CNT, etc. [156]. This technique is highly responsive to the orientation, material crystalinity and temperature. It depends on the interaction of inelastic scattering of monochromatic light with materials, and usually, a laser in the near ultra-violet, visible or near infrared range is used as the light source [107]. This can be used for molecules without a dipole moment. Raman spectrum of GO usually shows two bands: one observed at about 1575 cm^{-1} (G band) implies the graphitic structure present in the carbon allotrope and other at about 1350 cm^{-1} (D band) that indicates the occurrence of the disorder in the structure. These D and G bands are also appearing in Raman spectra of CD [107]. Further, this tool is also important for the characterization of different metal/metal oxide nanoparticles and CD/metal oxide-based nanohybrid.

X-ray photoelectron spectroscopy (XPS)

XPS is a surface chemical analysis technique that provides information on surface elemental composition and oxidation state of the elements. An XPS spectrum is measured by the number of electrons and kinetic energy upon irradiating the material with X-ray beam [213-217]. For the characterization of CD, XPS has generally been used for the assessment of the elemental composition and the chemical bonds of CD in combination with FTIR [156]. The incorporation of heteroatoms such as Al, Mg and Ni in CD cannot be detected by FTIR, but are detected by this technique [218, 219].

1.4.3. Diffraction technique

X-ray diffraction (XRD)

It is an efficient tool for the characterization of nanomaterials and polymeric nanocomposite, which provides information about crystal structure and degree of crystallinity. The crystal structure of the nanomaterial can be identified after measuring the angles and intensities of the diffraction peaks. The formation of metal and metal oxide nanoparticles is confirmed from their specific crystallographic peaks from XRD analysis [213]. The intensity of the crystallographic peaks of the nanoparticles is diminished after the formation of metal or metal oxide-based polymer nanocomposite owing to the occurrence of different chemical and physical interactions with the polymer matrix [214]. Further, it is also a vital tool to examine the interlayer spacing which calculated from the shifting position of the peak using Bragg’s equation, $2d\sin\theta = n\lambda$, where d, θ, n and λ are interlayer distance, diffraction angle, the order of diffraction and wavelength of X-ray respectively [181]. In addition, it also provides the information about the purity of CD [215]. The phase identification is done by analyzing the XRD data by comparing the inter-planar distances and values of intensity with the standard peaks using JCPDS files. Both small angle (less than 5°) and wide angle (2-90°) X-ray diffraction techniques are used to obtain microstructural features of nanomaterials or nanocomposites. Wide angle XRD provides information about the degree of crystallinity and nature of ordering arrangement, while the small angle is utilized to gain an idea on the size and shape of crystalline regions [216].

1.4.4. Microscopic techniques

Scanning electron microscopy (SEM)

SEM micrograph is predominantly used to visualize the surface morphology and dispersion patterns of different nanomaterials in the polymeric matrix. It constructs surface images of the material by scanning with focused electrons beam [220]. The electrons interact with atoms present in the material that generates various signals by emitting secondary electrons which are detected by a detector. These secondary electrons provide information on surface topography and phase composition of the samples [221].

Transmission electron microscopy (TEM)

TEM is the most imperative tool to view the actual structure and state of dispersion of the nanomaterials inside the polyester matrix as well as to authenticate the shape, size and aspect ratio of the nanomaterials. It permits a beam of electrons to transmit through the ultrathin specimen, which provides an internal structure of the sample [222]. Thus, TEM can provide direct observation of uniform distribution of GO and CD as well as atomic resolution lattice images [108]. Further, well dispersion of these nanomaterials in the polymer matrices can confirm by this technique [200]. The presence of different nanomaterials on the surface of CDs can be easily investigated in CD-based nanohybrid by this technique. Selected area electron diffraction (SAED) offers information about micro-diffraction patterns, inter-planar distances, and the symmetry of the lattice and crystal planes of the nanomaterials [156].

Energy Dispersive X-Ray Spectroscopy (EDX)

It is another frequently used technique for the chemical characterization and elemental analysis of a sample. EDX of CD provides the information about elemental composition such as the contents of carbon, oxygen and other doped elements like S, N, Si, P, etc. [157]. It is also very important to confirm the presence of different metals in the case of metal oxide- based nanomaterials. In addition, it can offer some information about the purity of CD.

1.4.5. Other techniques

Thermogravimetric Analysis (TGA)

The thermal stability of polymer, nanomaterial and polymeric nanocomposites are measured with the help of this technique. It analyzes the pattern and kinetics of degradation, char residue, etc. and the thermogram is normally obtained by monitoring the variation of the weight of the material with temperature due to decomposition, oxidation or loss of volatiles [48].

Differential Scanning Calorimetry (DSC)

Another important instrument to study the thermal properties of the polymeric materials is DSC. This tool is employed to measure melting temperature (T_m), T_g, kinetics of the reaction, crystallinity, amount of endothermic or exothermic energy, etc. [10].

1.4.6. Analysis and testing method

Mechanical test

Mechanical properties like tensile strength, modulus and elongation at break of pristine polyester and its nanocomposites are measured by Universal Testing Machine (UTM, at particular jaw separation speed). This test is usually performed according to standard ASTM D 882 method on rectangular film samples. Further, scratch hardness tester is used to measure the scratch hardness of the material by following the standard ASTM G 171 method. The impact strength of the material is measured using an impact tester by falling ball method (as per ASTM D 1709 method). UTM is also used to measure the lap-shear tensile adhesive strength.

Rheological study

The rheological study is usually performed with the help of a rheometer using a parallel plate in both steady shear and oscillatory modes. This study is carried out in order to determine the viscous and elastic components of polymer nanocomposite in terms of storage ($G^{/}$) and loss modulus ($G^{//}$), which consecutively facilitate in the determination of a state of dispersion of nano-reinforcing agents in the polymer matrix.

Chemical resistance test

The chemical resistance of polyesters and their nanocomposites are carried out in different chemical environments as per the standard ASTM D 543-67 method.

Biological tests

Biodegradation

Many standardized tests are available for evaluation of biodegradation of polymeric materials. One of the most suitable methods for evaluation of the biodegradability of materials is soil burial test where microorganisms present in the soil utilized for biodegradation by enzymatic action under suitable conditions. In outdoor soil burial test, the specimens were obscured in compost soil outside the laboratory in an open area whereas the indoor experiment was performed in the laboratory in plastic boxes consisting of compost soil. In both the experiments, biodegradability is evaluated based on weight loss of the films in a soil environment and SEM micrographs of films surface after the test. The 20% moisture is maintained in the soil by adding water to preserve the microorganisms, while specimens are buried at a depth of 5 cm [223, 224].

Another method is McFarland turbidity method where different types of bacteria are inoculated in a salt medium in the presence of tested film samples at 37 °C for a long period (30-60 days), and the bacterial growth in the medium is signified by the enhance in turbidity of the culture medium. Further, growth profiles of the bacterial medium are examined by UV-visible spectrophotometer using the intensity optical density (OD) at 600 nm at intervals of every 7-15 days complemented by weight loss profile of polyester [225]. In enzymatic degradation, the weight loss profiles of polyester and its nanocomposites is evaluated by immersing the samples in a buffer solution (maintaining optimum pH) containing commercial enzymes. Further, the degradation in phosphate buffer with or without enzymes is also evaluated as per the standard ASTM F 1635-04 method.

Hemolytic assay

The hemolytic assay is performed to get the preliminary information about the cytocompatibility of polyester matrix. The idea is to examine lysis of the red blood cell (RBC) in the presence of the tested polymeric material. The hemoglobin concentration was determined by measuring the UV absorbance intensity at 540 nm [226].

Antibacterial activity

Antibacterial test of polyester nanocomposites is mainly carried out by well diffusion method by measuring the colony formation unit and zone of inhibition. In a typical test, gentamicin is taken as the positive control, while 10% dimethyl sulphoxide as the negative control. In this method, test microbes are cultured on the Muller-Hinton agar or potato dextrose agar, placed in Petri dishes. The dispersed nanocomposites are placed into wells of 6 mm diameter on the Petri dish. In one well, a standard antibiotic is always used as the positive control. Then the zone of inhibition diameter is measured by the help of a transparent ruler upon incubation for 24 to 48 h at 37 °C [225, 227].

1.5. Property

Polymer nanocomposites reinforced with nanosized particles not only improves their mechanical, thermal, electrical, etc. properties but also introduces some fascinating properties. Some of the significant properties of polymers especially polyesters as well as their nanocomposites with different types of nanomaterials are discussed in this section.

1.5.1. Mechanical

Mechanical properties are one of the most imperative properties of polymers. The improvement in mechanical properties such as tensile strength, toughness, elongation at break, modulus, scratch hardness, etc. are observed in different polymer nanocomposites with the very low loading of nano-reinforcing agents [228]. Polyesters are highly flexible, but their mechanical properties including tensile strength are very poor. Designing of these polyesters by introducing some rigid aromatic moieties in their structure as well as unique hyperbranched structure improved the desired mechanical properties [229]. The non-entangled tree-like architecture with a large number of end functionalities offered better dense three-dimensional structures compared to the linear analog and resulted in high tensile strength, stiffness, hardness, etc. [57]. Further, the literature reported that the mechanical properties of polyesters were significantly enhanced by the incorporation of various kinds of nanomaterials like clay, GO, CNT, RGO, etc. Lee *et al.* [230] fabricated aliphatic polyester nanocomposites using two types of nanoclays (Cloisite 30 B and Cloisite 10 A) and found that Cloisite 30B-based nanocomposite showed higher tensile strength and modulus than Cloisite 10A. This is because of strong hydrogen bonding between aliphatic polyester and Cloisite 30B, and further confirms the significance of the strong interaction between polymer and nanomaterials in the formation of nanocomposites. Similarly, the incorporation of montmorillonite clay in the polyester matrix also showed noticeable improvement in tensile strength of pristine polyester and the value increased from 1.96 to 6.98 N/mm upon loadings of clay from 0 to 5 wt%. This is attributed to homogeneous dispersion clay delaminated by the polymer chains as well as after delamination large surface of the silicate layers are offered for substantial interaction with the polymeric chains which contributes to enhancement in tensile strength. Further, the elongation at break also increased with the increase in the loading of clay due to the existence of lengthy hydrocarbon chains of the fatty acids as well as the internal bond strength rather than cross-link density. As a consequence of enhancement in elongation at break and tensile strength, the impact strength is also improved [195]. Further, carboxyl and amino groups terminated aromatic HPEs functionalized MWCNT reinforced epoxy showed enhancement in tensile strength and elastic modulus. This is due to the reinforcing effect of MWCNT which is improved after non-covalent functionalization method. The functionalized MWCNT are uniformly and individually dispersed in the epoxy matrix can tolerate load more efficiently as well as the flexible HPE present on the surface of functionalized MWCNT can mitigate stress by deformation at the interface and thus help in bearing load more consistently [231]. Selim *et al*. [232] reported that improvement in their mechanical properties including impact resistance (18J) and bending by introducing ZnO into sunflower oil-based environmentally benign hyperbranched alkyd. The tensile strength of blend nanocomposite of epoxy and polyester with graphene nanoplatelets also attained around 86.8% with inclusion of only 0.2% of the nanomaterials compared to the pristine epoxy/polyester [233]. The incorporation of 3 wt% RGO into unsaturated polyester resulted in 76% enrichment in tensile strength (54 MPa) in contrast to pristine one (25 MPa), and the value further increased with the loading of RGO. However, elongation at break decreased gradually from 80% to 47% for 3 wt% loading of RGO [234].

1.5.2. Thermal

HPE exhibit high thermal stability compared to linear analogs due to their three-dimensional cross-linked architecture with bulky numbers of functional groups [235]. Further, fabrication of polyester nanocomposites with various kinds of nanomaterials likes clay, RGO, CNT, GO, etc. enhanced the thermal properties and copious studies have been carried out on these. These nanomaterials are acting as the thermal insulator as well as the mass transport barrier which increases the overall thermal stability and help in the generation of char after thermal decomposition. This also confines the thermal motion of polymer chains and delays the release of VOC [81]. Bastiurea *et al.* [236] reported that polyester nanocomposite with 0.1 wt% graphite showed the initial mass loss at 307 °C and 50 % loss was observed at 385 °C. However, for polyester with 0.1 wt% GO mass loss started at 320 °C, and 50% mass loss was noticed at 390 °C. Further, GO-based unsaturated polyester nanocomposite showed remarkable improvement in thermal stability from 230 to 285 °C [19]. An improvement of thermo-stability of the polyester nanocomposites was also observed upon incorporation of nanoclay. The onset thermal degradation temperatures of the pristine polyester were increased from 5 to 18 °C on the incorporation of 1 to 5 wt% clay into it. This may be owing to the interaction of clay with polymeric chains which can instantly change the chain kinetics near the platelets [11]. Further, improvement in T_g of polyesters after formation of the nanocomposites was also reported in the literature. Bora *et al*. [19] reported that T_g of polyester increased gradually from 54 °C to 62 °C on the incorporation of RGO into the polyester matrix. Bastiurea *et al*. [236] demonstrated that GO-based polyester nanocomposites exhibited higher T_g than graphite-based nanocomposite. Further, an introduction of GO in poly(butylenes succinate) also demonstrated a shifting of T_g from 28 °C to 208 °C, at a loading of 1- 2 wt% GO [237].

1.5.3. Barrier

The improvement in gas barrier properties of polymers is also observed after incorporation of different types of nanomaterials into them. This can be described by the fact that the nano-reinforcing agents cause the tortuous diffusion paths for the gas molecules to follow and hence there is a reduction in diffusion rate [81]. Ahmadizadegan *et al.* [196] reported that addition of cellulose/silica into polyester matrix follows the gases permeability in the order of PO_2 (98%)>PCO_2 (88%)>PN_2 (58%)>PCH_4 (38%). The separation efficiency of carbon dioxide/nitrogen and carbon dioxide/methane gases was also improved after formation of the nanocomposite and the diffusion coefficients of gases enhanced with the increase in mass fraction of cellulose/silica in the membrane. Charlon *et al.* [237] reported that lower permeability of gases in comparison with the unfilled poly(butylene succinate)-based membranes. Thus, superior barrier properties of the polyester nanocomposite membranes are mostly described by a rise of the diffusion pathways influenced by the incorporation of nanomaterial.

1.5.4. Electrical

Electrical properties of polymers are usually related to dielectric and electrical conductivity. Presence of a graphene sheet can offer percolated pathways for electron transfer in the nanocomposite, which makes the nanocomposite electrically conductive. Similar types of results can be achieved by utilizing other carbon-based nano-reinforcing agents such as carbon nanofibers, CNT, graphene, etc. However, graphene allows the transition from insulator polymer to a conductor at significantly lower loading, compared to CNT [238]. Battisti *et al*. reported the electrically conductive thermosetting polyester/CNT nanocomposites by AC impedance spectroscopy and DC conductivity measurements. The enhancement in electrical conductivity was reported for graphene nanosheets-based poly(butylenes succinate) nanocomposite. The electrical conductivity was enhanced from 3.32×10^{-9} to 2.05×10^{-3} S/cm by 5 wt% graphene loading, which demonstrating about 10^6-fold enhancement. This progress can be ascribed to the formation of interrelated conducting networks produced by graphene nanosheets in the polyester matrix [239]. Binti and Raja [240] demonstrated improvement in electrical conductivity of poly(butylenes succinate) nanocomposite after addition of CNT.

1.5.5. Rheological

The study of the rheological properties of every polymeric material is vital to achieve fundamental perceptive of the processibility of the materials. Rheology is actually the study of the deformation and flow of matter under the influence of an applied stress and conducted either by steady shear or dynamic oscillatory shear measurements [11]. Steady shear sweeps were utilized to explore the flow properties of polymers by determining the viscosity with increasing shear rate. Further, the viscoelastic properties like loss and storage moduli display phase transition behavior upon formation of nanocomposites from liquid-like to solid-like. Shear viscosity of nanocellulose reinforced polyester nanocomposites showed two different regions shear thinning and Newtonian flow, whereas the pristine polyester showed only Newtonian behavior. With the incorporation of nanomaterial, the reinforced systems showed strong shear thinning behavior where at low shear region viscosity is found to decrease with increasing shear rate. Even at 0.5 wt% loading of nanocellulose leads to enhancement in shear viscosity of the nanocomposite due to strong particle-particle interaction [241]. The storage modulus of the vinyl ester-polyester resin suspensions with MWCNT and MWCNT-NH_2 demonstrated pseudo solid like behavior, which is independent of frequency; particularly at low frequencies, at 0.3 wt% of loading. Furthermore, the values of the loss modulus of the suspensions were increased with an increase in loadings of CNT [242]. Clay- based polyester nanocomposite fabricated by Konwar *et al.* [11] showed higher zero-shear viscosities and shear thinning behavior compared to the pristine at loading of 1–5 wt% clay. Further, 12% enhancement in storage modulus was observed for poly(butylene succinate) nanocomposite on the incorporation of 2 wt% GO [239].

1.5.6. Optical

Polymer nanocomposites with optically active functional groups show different interesting optical properties including transparency, fluorescence, refractive index, luminescence, etc. Generally, polyester thermosets are highly transparent in nature and transparency of these thermosets is not affected significantly after the formation of nanocomposites. This is owing to the low scattering of light by the well-dispersed nanometer size particles as well as the presence of a very minute amount of nanomaterials. Zhao *et al.* [12] reported that ZnS-based acrylated HPE nanocomposites with the transparency of > 91% at the wavelength of 500 nm with different loadings of ZnS. Further, unsaturated polyester nanocomposites showed good transparency with 1 and 3 wt % loadings of sepiolite clay due to good dispersion of the sepiolite in the matrix [243]. In addition, interesting optical properties including luminescence is observed by incorporating nanomaterials like quantum dots and metal nanoparticles into polyesters. Mosconi *et al.* [20] reported CD-based poly(ester amide) nanocomposite with a remarkable change in PL properties. It is reported in the literature that PL of CD solution could be quenched effectively by the presence of electron acceptor or even donor molecules. Thus, the photoexcited CD together with excellent electron donors and acceptors recommend for their feasible use in photocatalytic application. Although no report was found on CD-based polyester nanocomposites, but one report was found on optical properties of fully bio-based aliphatic HPE, synthesized from glycerol and adipic acid as well as glycerol and succinic acid. These HPE show blue color under UV light and PL emission upon exciting at different wavelengths. The clumping of the carbonyl groups is accountable for this clustering-induced emission [244].

1.5.7. Biodegradation

Biodegradation involves the breakdown of the polymeric materials into oligomeric fragments of low molecular-weight in the presence of microorganisms/ PBS/ enzymes, followed by mineralization. One of the prominent aspects of aliphatic polyesters contributing towards global sustainability is that they are susceptible to microbial attack because of the existence of hydrolyzable ester bond in their main chains. A typical biodegradation process comprises four main steps, i.e., absorption of water, cleavage of ester linkages and generation of oligomeric fragments, solubilization of such fragments, and ultimately engulfment of soluble oligomers by the exposed microorganisms. Therefore any factor which influences the hydrolysis tendency may control the biodegradation process. Further, significant improvement in biodegradation is reported in literature after formation of polyester nanocomposites. The result of improvement may be attributed to the catalytic role of the nano-reinforcing agents by biodegradation process. Konwar *et al*. [11] reported the dose- dependent enhancement of biodegradation of highly branched polyester of *Mesua ferrea* L. seed oil against *P. aeruginosa* and *B. subtilis* bacterial strains upon loading of nanoclay.

1.5.8. Antibacterial

The inclusion of biocidal agents into polymeric nanocomposites has contributed to the growth of versatile antibacterial materials that are valuable for a wide range of biomedical, packaging, etc. applications. Generally, pristine polyesters do not exhibit antimicrobial activity, but the incorporation of different metal or metal oxide nanoparticles like, Ag, Cu, TiO_2, CuO, ZnO, etc. into them resulted in excellent antibacterial activity. Sun *et al*. [245] reported Ag nanoparticle-based polyester nanocomposite with good antibacterial activity (96%) against *Stapphylococcus aureus* and *Escherichia coli* with the low content of nanomaterials (100 ppm). Cellulose /silica-based polyester bionanocomposite also showed antibacterial activity against *E. Coli.* and *Bacillus's cereus* [196]. In accordance to numerous research studies, it is established that electromagnetic attraction occurred between the microorganism and nanoparticles as they contain the positive charge and the microorganism carries the negative charge. This leads to the death of the microorganism [246, 247].

1.5.9. Catalytic

Most interestingly photocatalytic properties can be introduced into polymers by incorporating different semiconductor nanomaterials like TiO_2, SnO_2, ZnO, CD, etc. These materials upon excitation of light generate electron/hole pairs and react with H_2O and O_2, to generate reactive oxygen species like $^{\cdot}OH$ and $^{\cdot}O_2^-$ which take part in the catalytic reactions. However, the necessity of ultraviolet light to stimulate such photocatalysts drastically limits their practical applications as the content of UV light in the solar spectrum is very low (about 2-3 %). In this regard, CD-based nanohybrid such as CD/TiO_2, CD/ZnO, CD/SnO_2, etc. showed extremely enhanced photocatalytic performance under visible light [181]. However, reusability and agglomeration problems of such nanomaterials need to be addressed. Thus, use of polymer nanocomposites as heterogeneous catalysts emerges as more efficient catalysts. Mahdieh *et al*. [248] fabricated a self-cleaning polyester/cellulose fabric by decorating metallic silver and TiO_2. The photocatalytic property of this material was observed by discoloring of methylene blue under sunlight and UV light. Photocatalytic properties of *in-situ* and *ex-situ* fabricated TiO_2 nanowires-based HPE nanocomposites were investigated by Ghanem *et al*. [14] by measuring the chemical oxygen demand (COD). COD analysis established the mineralization of waste material through photocatalytic degradation at an enhanced rate. N-doped CD-based polyester-amide nanocomposite fabricated by Mosconi *et al*. [20] was used as a heterogeneous photocatalysis for the synthesis of benzaldehyde by greener oxidation of benzyl alcohol under visible light. They exhibited good photocatalytic activity towards the oxidation and offering a new scenario for their prospective application in the photocatalytic field. Many reports are available on photocatalytic activity of CD-based metal oxide nanohybrid and their different polymer nanocomposites including epoxy, poly(vinyl alcohol), polyurethane, etc. De *et al*. [107] reported that CD reduced Cu_2O nanohybrid-based epoxy nanocomposites showed excellent photocatalytic activity (90%) with good reusability towards degradation of a pesticide under visible light. Polyester fabric with self-cleaning activity under visible light was developed by Gaminian *et al*. [249] through *in-situ* synthesis of Cu_2O doped TiO_2 nanohybrid toward indoor self-cleaning applications. Cu_2O/TiO_2-treated polyester fabrics exhibited considerable photocatalytic activity towards photodegradation of methylene blue on exposure of sunlight after three washing cycles.

1.6. Applications

Polyesters and their nanocomposites owing to their superior properties such as mechanical, thermal, barrier, electrical, optical, etc. have shown ubiquitous presence in various fields of applications. Thus, this section tried to highlight different advanced applications of such polymeric materials.

Coatings and paints

Polyesters are explored for a wide range of industrial applications including surface coatings, adhesives, paints, laminates, etc. [10]. They are also used to make films, automotive interiors, holograms, capacitor components, wire insulation, jet engine seals, tapes, textiles, liquid crystal displays, etc. [11]. High functionality combined with the low solution viscosity of HPE brings interest for the application of these materials in coatings as a multi-functional cross-linker [115]. A HPE based on 4,4-bis(4-hydroxyphenyl)pentanoic acid was used in UV curable coating with cationic photoinitiator [250]. However, the adverse effects of VOC on the atmosphere have focused research for the coating industries towards eco-friendly solution comprising materials with high solid contents and low solvent. Thus, approaches for designing advanced nanomaterials and hyperbranched architectures have gained significant interest. In addition, sustainable resource-based VOC free coatings with superior anticorrosive properties are the most demanding materials in the surface coating industry. Pathan *et al*. reported that butylated melamine formaldehyde cured castor oil-based waterborne alkyd using an environmentally friendly solvent with anticorrosive properties [77]. Similarly, sunflower oil-based eco-friendly hyperbranched alkyd resins with well dispersed ZnO nanospheres improved the mechanical properties, durability and anticorrosive features of the nanocomposites and thus demonstrate potential applications for eco-friendly surface coatings [231]. Verma *et al*. [251] developed poly(dimethyl siloxane) modified polyester-based waterborne, thermally cured hydrophobic coating to be employed in corrosion protection of copper using hexa(methoxy methyl)melamine as a cross-linker. This siloxane modified coating exhibited enhanced mechanical and electrochemical properties along with outstanding hydrophobicity, as compared to the pristine polyester coating. Waterborne polyesters are also extensively used in wood, plastic, architectural and metal coatings, printing inks, etc.

Further, various kinds of nano-reinforcing agents such as nanoclay, metals nanoparticles, etc. are incorporated into the polyester matrix to gain highly hydrophobic, antimicrobial, high performance, thermostable and flame retardant surface coating materials. In addition to surface coating materials, they are also used as adhesive and sealant. Fogelstrom *et al*. [252] designed hard and flexible coatings with improved flexibility, surface hardness and scratch resistance as well as excellent adhesion and chemical resistance by introducing montmorillonite in HPE resin.

Electromagnetic interference (EMI) shielding

Another promising application of polyester nanocomposites is electromagnetic interference (EMI) shielding. Different carbon-based nanomaterials such as graphene, carbon black, graphite, CNT, carbon nanofiber, etc. are used to improve EMI shielding efficiency of polyesters. Gnidakouong *et al*. gained EMI shielding efficiency from 30 MHz to 1.5 GHz for MWCNT-based unsaturated polyester nanocomposite [253]. Similarly, 20 wt% MWCNT- based polyester nanocomposite exhibited EMI shielding efficiency of 18 GHz better than 1 wt% loading (8.2 GHz) [254].

Biomedical

Further, polyesters due to their superior physical properties found applications in biomedical fields. Many reports are available on synthesis of polyesters using different polyols such as 1,8-Octanediol, butylene glycol, ethylene glycol, glycerol, castor oil, etc. and carboxylic acids such as ricinoleic acid, sebacic acid, citric acid, etc. which find applications in soft tissue engineering as tissue adhesives, drug delivery and scaffolds to renovate or replace body tissues [60]. Poly(polyol sebacate)s obtained from polyols and sebacic acid; are good candidate to build up degradable materials, owing to their combination of degradability and flexibility, which are precious properties in the milieu of soft-tissue engineering [255]. A highly flexible polyester, poly(1,8-octanediol-citrate) was designed as an outstanding material in tissue engineering and the material is hydrophilic, elastic and porous. Moradi *et al*. [256] developed a porous scaffolds material by incorporating hydroxyapatite microparticles into citric acid-based polyester elastomer through an effective route which find possible applications in tissue engineering. Further, carbon-based nanomaterials are proved as useful reinforcing agents for polyesters in biomedical engineering owing to their biocompatibility, non-toxicity, cytocompatibility, improved erosion resistance, etc. [257]. Chemically modified graphene and GO enhanced *in vivo* interaction with cells and proteins and hence improving the cell proliferation and adhesion [258]. CNT reinforced biodegradable poly(1,8-octanediol-citrate)-based polyester fabricated by Meng *et al*. [259] had a lower swelling and weight loss compared to the pristine polyester. Cytotoxicity and incubation tests demonstrated that the loading of CNT increased the in vitro biocompatibility and bovine serum albumin adsorption hydrophilicity of the nanocomposite.

Self-cleaning material

Recent times, instigating self-cleaning properties on polymeric materials under irradiation of visible light for automotive applications is in a crucial point of research, which can be achieved by incorporating metal-doped TiO_2 nanoparticles into polymer matrices. Gaminian *et al.* developed a polyester fabric with Cu_2O doped TiO_2 nanoparticles, which is visible light active self-cleaning [249].

Miscellaneous

Furthermore, polyester nanocomposites are designed with carbon-based nanomaterials to find applications in various fields like supercapacitors, fuel cells, textiles, etc. These nanocomposites seem to be low cost but versatile as futuristic advanced industrial materials. Flexible supercapacitor based on CNT coated polyester was fabricated by Huang *et al.* and it showed excellent specific capacitance (15.67 cmF/cm^2) as well as 90% stability after 1000 cycles and exhibited optimum power supply for wearable electronic devices [260]. The textile industry is also interested in carbonaceous nanomaterials-based polyester nanocomposites. Smart e-textiles with high performance can be created using graphene, CNT, etc. coated polyester fibers. Molina *et al.* demonstrated that electrical properties were also changed after incorporation of GO into the polyester matrix [261]. Recent research showed that reinforcement of GO in polyester improves its hydrophilicity as well as antistatic properties. Thus, research on GO-based polyester nanocomposite showed a new path to produce engineered materials and practical devices for numerous applications [262].

Most interestingly, the development of a new kind of CD-based polymer nanocomposites permits to control the fundamental properties through size and shape effects. These special properties include PL, anti-reflecting, anti-icing, anti-fogging, anti-counterfeiting, anti-graffiti, etc. as well as catalytic activity. However, these properties were not explored extensively so far for these polyester nanocomposites.

1.7. Scopes and objectives of the present investigation

It has been seen from the above discussions of the earlier sections that several works have already been performed on renewable or non-renewable resources-based polyesters as well as their nanocomposites. However, WHPE is not explored to that extent, and their nanocomposites are very rare in the domain. In most of the literature, solvent-borne polyester is utilized for the fabrication of polyester nanocomposites, and thus drawbacks related to waterborne polyester were not addressed. Further, literature remains silent on the fabrication of CD- and GO-based WHPE nanocomposites, especially from renewable resources. CD is a fantastic material of this era with various unique properties, and thus it may offer some unique attributes to the resultant polyester nanocomposite. Therefore, a superiority of CD concurrently with bio-based waterborne polyester is yet to be explored. Thus, it unlocks a fresh area of research on CD- and GO-based WHPE nanocomposites which offer low-cost and versatile materials for multifaceted applications but also very valuable concerning the current development of advanced materials. In this vision, the bio-based WHPE nanocomposites which are imagined as one of the solutions to compel in the revolutionary advance material science field have flash up with the following queries.

(1) Whether WHPE can be synthesized from bio-based raw materials without using any solvent and catalyst?
(2) Whether water solubility can be achieved without using any neutralizing agent?
(3) How much advantage can be achieved from bio-based waterborne polyester compared to solvent-borne polyesters?
(4) Whether nanocomposite can be fabricated in the absence of solvent and compatibilizing agents without any aggregation?
(5) Whether properties of waterborne polyester can be improved by incorporation of functionalized as well as non-functionalized nanomaterials?
(6) Whether the nanocomposites will remain biodegradable like pristine polyester or not?
(7) Whether such nanocomposites could find applications in any advanced field or not?

Thus, encouraged by the above-mentioned scopes the main objectives of the present investigation are made as follows:

(1) To synthesize WHPE using bio-based raw materials.
(2) To characterize the synthesized polyester using various spectroscopic and analytical techniques.
(3) To evaluate different properties including physical, mechanical, thermal, chemical and biodegradability as well as biocompatibility of synthesized waterborne polyester.
(4) To prepare and characterize different carbon-based nanomaterials like GO and CD and CD-based nanohybrids.
(5) To fabricate different nanocomposites by incorporating various nanomaterials such as GO, CD, CD/TiO_2, and CD/clay into the WHPE matrix.
(6) To characterize and evaluate different physical, rheological, mechanical, thermal, biodegradable and antimicrobial properties of the prepared nanocomposites.

(7) To optimize the performance characteristics of the nanocomposites by scrutinizing the dose level of nanomaterials to achieve the best material for various possible applications.

1.8. Plan of the present work

In order to execute the proposed objectives, the research work is planned in the following ways:

(1) A thorough state-of-art literature survey in the field of polyesters, bio-based waterborne polyesters and their nanocomposites, GO, CD and CD-based nanohybrids will be conducted.

(2) Bio-based WHPE will be synthesized by a polycondensation reaction in the absence of additional solvent, catalyst and neutralizing agents.

(3) The synthesized polyester will be characterized by different analytical and spectroscopic techniques such as FTIR, NMR, TGA, DSC including determination of acid value, saponification value, hydroxyl value, etc.

(4) The physical, mechanical, thermal and chemical properties, as well as biodegradability and biocompatibility of the synthesized polyester, will be evaluated by the standard methods.

(5) CD will be prepared from bio-based raw materials through the one-pot hydrothermal protocol and will be characterized by different spectroscopic techniques.

(6) Different CD-based nanohybrids will be prepared by the one-pot hydrothermal protocol.

(7) WHPE nanocomposites will be fabricated using above nanomaterials by the *in-situ* polymerization techniques without using any solvent and compatibilizing agents.

(8) The fabricated nanocomposites will be characterized by different spectroscopic techniques and surface morphology with state of dispersion will be studied by using SEM and TEM.

(9) The mechanical, thermal and chemical properties of the nanocomposites will be evaluated by the standard methods.

(10) The biodegradability and antibacterial activity of the nanocomposites will be tested.

(11) Optimization of the performance characteristics of the nanocomposites will be completed by monitoring the dose level of nanomaterial to gain the best material for potential multifaceted applications.

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