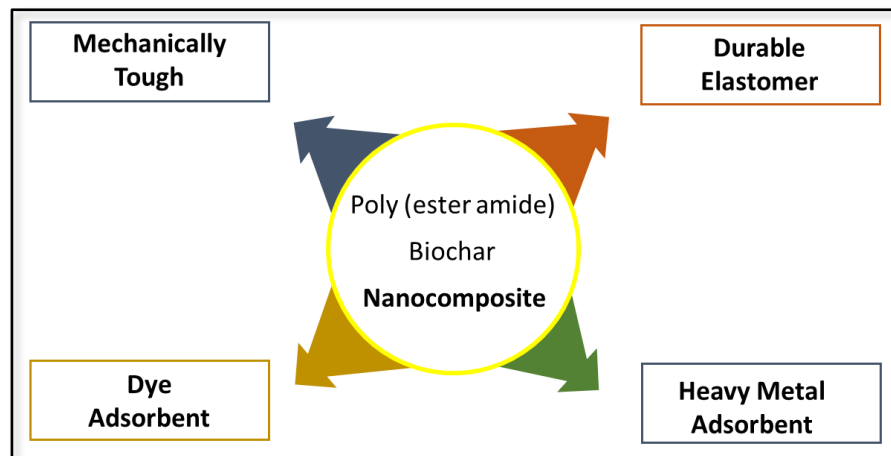


# Chapter 1



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**General Introduction**

***Highlights***

This chapter delves into an in-depth exploration of the fundamental aspects of poly(ester amide)s and their nanocomposites derived from bio-based materials. It encompasses a brief overview on several core elements, inclusive of the structural compositions of poly(ester amide)s, the materials and methodologies used in carrying out their synthesis, the techniques engaged for characterization, the evaluation of their properties followed by their potential applications. In addition, this chapter demonstrates the production of different poly(ester amide) nanocomposites utilizing various carbon-based nanomaterials, particularly nanoclay, carbon nanotubes, biochar, modified biochar, etc. In turn, the chapter also provides a comprehensive discussion on different spectroscopic, analytical, and microscopic methods exclusively employed to conduct characterization of various nanomaterials, nanohybrids, and poly(ester amide) nanocomposites. Additionally, this chapter showcases upon how the quantity and type of reinforcing agents can influence the performance attributes of these poly(ester amide) nanocomposites. The chapter also touches down the aspect of manifold prospective applications exhibited by these poly(ester amide)s and their nanocomposites in the domain of material science and technology. In culmination, it outlines in detail the scopes, objectives as well as plan of the current research.

## **1.1. Introduction**

Since the advent of prehistoric times, along with a walk into the annals of scientific history, it has been found that polymers have steadfastly procured an irreplaceable position in the material realm. They are known to exert their influence in both economic as well as industrial vantage units. On account of their ubiquitous nature, they have found their extensive applications in multitude aspects, viz., packaging, coating formulations, adhesives, sealants, electronic sectors, foam materials, automobile industries, biomedical sectors, etc. [1] Over the passage of recent times, a thorough and elaborate scrutiny on the intrinsic features of these polymeric materials, which account for their versatility, has resulted in facilitating evolution of their traits coupled with fostering significant advancements in their utility as prime materials [2, 3]. However, the heavy dependency on these synthetic polymers, which are sourced primarily from conventional resources, viz., petroleum reserves, induces pressing sustainability issues. Moreover, the diminishing availability of these non-renewable sources of energy, particularly, the petroleum stocks in conjunction with their association to release of greenhouse gases further intensifies the intricacies related to the challenging task of environmental conservation [4]. In light of the burgeoning global population, the mounting consumption of these man-made polymers underscores the urgency for responsible utilization as well as effective disposal techniques in order to carry out mitigation of the potential ecological risks [5, 6]. In order to tackle these formidable constraints and address the disposal issue, scientists from across the globe have explored the notion of conferring biodegradability traits to these synthetic polymers [7]. Howsoever, this evolves as a difficult endeavor to achieve biodegradability in these polymers which are mostly derived from petroleum reserves. As a result, there is an escalating demand to confront these environmental issues and bolster the level of sustainability of polymers by carrying out investigation of bio-based feedstocks which are renewable in nature and can serve as viable alternatives to petroleum reserves [8-10]. While the adoption of such bio-based precursors present numerous advantages conducive to the environment, the processes generally invoke the usage of solvents which can cause emission of certain noxious compounds into the atmosphere, particularly the volatile organic compounds (VOCs), thereby leading to environmental degradation [11]. Under this context, bio-based waterborne polymers come into action as eco-friendly alternatives to synthetic polymers. These polymers use water as the prime solvent, thereby offering diverse benefits, viz., non-flammability, non-toxicity, ease of cleansing, minimal or no

VOC emissions, and absence of odorous species, etc. [12]

Amidst the wide spectrum of synthetic polymers, poly(ester amide)s stand out as an important class of polymers owing significant importance. They portray a principal role within the realm of materials science, on the ground of their unique chemical topology that seamlessly facilitates the union of ester as well as amide functional groups in the polymeric network. This distinctive structural architecture of duality bestows excellent versatility, thereby permitting meticulous tailoring of chemical as well as physical traits via precise selection of monomer units and proper alterations of different compositions. On ground of their prized versatile nature, these polymers find extensive applications in various domains ranging from protective coating formulations, sustainable packaging materials to biomedical usage, viz., controlled drug delivery units, biodegradable sutures, tissue engineering scaffolds, etc. [13, 14]. These polymers are primarily synthesized via polycondensation reactions which are meticulously designed and involve the reaction between diacids, diols and diamines. The in situ generated monomers from these starting materials undergo a series of condensation reactions to yield the polymer bearing ester as well as amide functional groups. This entire process involves unambiguous tailoring of the polymeric framework and its properties, thereby making it apt for its utility in manifold fields. Under light of these considerations, it is noteworthy that all these monomers can be sourced from different bio-derived raw materials. This throws light on the eco-friendly as well as sustainability nature of these polymers, thereby enabling an economically viable technique of fabrication [15]. In addition, the ability to invoke water as the solvent in carrying out the fabrication of poly(ester amide) material goes hand in hand with the environmental friendly attribute of the synthetic route of preparation. In this vein, bio-based poly(ester amide)s which are waterborne in nature pose as a great alternative to conventional solvent borne poly(ester amide)s, derived mostly from petroleum resources. This shift towards the usage of bio-derived polymers not only syncs with the principles of Green Chemistry but also underscores the requirements of sustainability in conducting the synthesis of polymers [12].

Despite the numerous pros exhibited by poly(ester amide)s, they do demonstrate certain intrinsic drawbacks. These limitations are inclusive of limited toughness values, low resistance towards alkaline environmental conditions, subpar tensile strength values, etc. These shortcomings of poly(ester amide)s limit their applications in various contemporary

domains [16]. In an effort to mitigate these limitations effectively, integration of nanomaterials into the main polymer matrix is carried out which results in the fabrication of polymer nanocomposites. Herein, the intricate dispersion of the nanomaterials into the main polymer matrix aids in fortifying the overall structure, thereby causing pronounced enhancement in the inherent properties of the material. Additionally, it was observed that these polymer nanocomposites generally outperform the conventional ones which invoke usage of micro reinforcing agents instead of nanomaterials [17, 18]. The incorporation of the former reinforcing agents results in achieving superior properties, viz., low density values, decreased weight, increased transparency levels, improved mechanical performance, etc. Therefore, it can be stated that nanotechnology portrays an extremely pivotal role in carrying out notable improvement in the performance characteristics of the poly(ester amide) nanocomposites. This further elicits considerable attention from research explorers across the globe to carry out significant exploration within this burgeoning genre in various advanced applications.

Till date, a vast array of various nanomaterials has been identified, each of them characterized by distinctive dimensions and shapes. Consequently, these nanomaterials are comprehensively categorized into various groups which are primarily inclusive of zero dimensional (0-D) entities, viz., nanospheres, nanodots, biochar, etc., one dimensional (1-D) configurations, viz., nanowires, nanotubes, etc., two dimensional (2-D) structures like nanosheets, etc. [19, 20] In turn, these nanomaterials are further categorized on ground of their origin, i.e., whether they emanate from inorganic or organic sources. It has been closely observed over the years that carbon-based nanomaterials stemming from organic precursors portray a paramount role in carrying out fabrication of various polymer nanocomposites due to their low toxicity levels, favorable thermal, chemical and physical attributes along with sustainable nature. Additionally, within this multitude class of nanomaterials, an assorted array of carbon-based nanomaterials persists which are inclusive of carbon dots, carbon nanofibers, biochar, etc. [21] Over the passage of recent years, fabrication as well as usage of biochar as a reinforcing agent in polymer matrices has garnered tremendous attention. In addition, biochar is known to serve a plethora of property enhancements, viz., thermal stability, flame retardancy, mechanical reinforcement, electrical conductivity as well as improved water and gas barrier traits. Under this purview, biochar is mainly generated using diverse lignocellulosic sources and waste materials such as rice husk, vegetable peels, cashew nut shells, saw dust powder,

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etc. [22-26] Suleman et al. in 2022 carried out the fabrication of biochar from castor leaves and the biochar material was subsequently utilized as an adsorbent material for conducting adsorption of safranin from wastewater generated from textile industries [27]. In a similar vein, Pipiska et al. in 2022 synthesized biochar material from corn cob as well as wood chips in order to facilitate the adsorption of fluorescent dyes, viz., Erythrosine B and Thioflavin T [28]. At the current juncture, integration of biochar into polymer matrices is comprehended as an economically viable alternative and has found profound application in numerous fields. Khan et al. in 2017 used biochar as a reinforcing agent in epoxy composites and its toughness values were compared with carbon nanotubes. It was ascertained that 2 wt% biochar loading provided superior toughness values in comparison to the latter [29]. Again, in 2015, Das et al. carried out integration of biochar particles into conventional polypropylene matrix. It was deduced that with regular increment in biochar content, there was rise in residual weight loss values, thereby highlighting enhanced thermal stability of the polymer composites [30]. Another study carried out by Zhang et al. in 2017 revealed that biochar addition helped in delaying the rate of heat degradation in polypropylene composites which in turn augmented the flame retardancy of the entire material [31]. Poulou et al. in 2018 studied the aftermath of biochar addition on the electrical conductivity values of the polypropylene/biochar composite and it was assessed that the addition resulted in shooting up the conductivity value by four times. There exists another prominent class of nanomaterials stemming from inorganic precursors, in addition to carbon-based nanomaterials. This distinctive category is inclusive of copper oxide (CuO), iron oxide (Fe<sub>3</sub>O<sub>4</sub>), zinc oxide (ZnO), nanoclay, viz., bentonite, montmorillonite, etc. These nanomaterials from inorganic origin portray a crucial role in bolstering the features of polymer nanocomposites. A comprehensive evaluation of the literature demonstrates the variegated array of polymer nanocomposites. These nanomaterials not only ameliorate the intrinsic traits of the crude polymer materials but also aid in introducing novel properties into them, thereby making them pertinent for conducting advanced applications in manifold contemporary realms [32-36].

Taking into consideration the current scenario of escalating demand for poly(ester amide)s and their nanocomposites across a wide spectrum of advanced contemporary applications, there persists a strong affinity towards craftsmanship of such materials bearing high-end performances as well as addressing issues pertaining to ecological compatibility and environmental sustainability. In this milieu, preparation of waterborne poly(ester amide)s

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and their nanocomposites using different renewable sources assumes a prolific role via an environmentally congenial route of preparation. This technique of fabrication not only renders sustainability feature to the materials, but also goes in perfect alignment with the cognizant principles of sustainability, thereby offering numerous properties well-suited for conducting manifold applications in various spheres.

## **1.2. Historical background**

The inception of polymer science can be dug down deep into its origin in various industrial units and scientific laboratories which was formally integrated into academic arena later on. The culmination of polymer science realm can be tracked down to the time regime when natural polymers, viz., cellulose encountered derivatization into celluloid as well as cellulose acetate, prior to coinage of the term “polymer” by the father of Swedish Chemistry, J. J Berzelius. This transformation of cellulose into its respective derivatives was carried forth by Henri Braconnot and his ancillary in 1830s. In turn, the synthesis of “bakelite” in 1907 by Leo Baekeland paved the way for the entry of synthetic polymers in the genre of material science. Following this, in 1922, a German chemist, Hermann Staudinger provided an elaborate and pivotal statement on polymer and its etymology. He revealed that polymers are primarily long extensive chains of small molecules or entities which are interconnected amidst each other via covalent bonds. This groundbreaking statement opened the doors towards synthesis of numerous polymers which are inclusive of polystyrene in the year 1929, polyesters in the year 1930, polyethylene and poly(vinyl chloride) in the year 1933, followed by synthesis of nylon in 1935 [37-40].

Poly(ester amide)s demonstrate an important significant category of polymers known for their exclusive ability to coalesce the premium features of polyesters, such as biodegradability and cytocompatibility, along with the excellent mechanical, thermal and stiffness attributes of polyamides. Over the years, these polymers have amassed widespread speculation on account of their versatile nature. They have found their utility in different consumable items under the trademark name, Bayer or BAK<sup>®</sup>. The preliminary synthesis of PEAs traces down to the year 1932 when Carothers successfully carried out the reaction between diols, diacids and diamines. In order to carry out exploration of polymer materials that merged both the traits of polyesters and polyamides, various ordered, random and block co-poly(ester amide)s were prepared by using different stoichiometric ratios of hexamethylene adipate and hexamethylene adipamide [41].

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Sheahan and Goodman in mid-20<sup>th</sup> century conducted this synthesis and further assessed their mechanical as well as thermal properties. This was followed by rapid advancements in the domain of polymer science and technology which summoned extensive versatility and customization of poly(ester amide) material. This led to exploration of various avenues of poly(ester amide) material by different techniques. Under this context, many research enthusiasts in 1974 studied the systematic transitions/relaxations of an entire series of linear poly(ester amide)s which were based on terephthalic acid and were consistently alternating in nature [42]. The detection was done by assessing the dynamic mechanical study and also some other thermomechanical studies. This assessment was conducted in a bulk scale in the department of fiber and textile of Snamprogetti, Saudi Arabia. Similarly, Haan and Gaymans carried out synthesis of segmented copolymers from poly(tetramethylene oxide) with a series of different poly(ester amide)s units bearing uniform chain lengths [43]. The end products were found to be highly melt processable without any deviations in original chain length behavior. Eventually, different new additives such as poly(butylene terephthalate) were added in poly(ester amide) copolymers to scrutinize as well as improvise the inherent properties of the material. Gaymans and Bennekom in 1997 assessed that incorporation of poly(butylene terephthalate) resulted in an increment of the crystallization behavior of the crude poly(ester amide) resin by multiple folds [44].

Over the years, hyperbranched poly(ester amide)s (HBPEA) have evolved steadily and they constitute a specialized category of polymers known exclusively for their highly branched and intricate molecular architecture. In 1995, the synthesis of HBPEA was first documented by Krischeldorf and his group. This reaction was conducted using 3,5-bis (3-acetoxybenzamide) acid via silyl activated polycondensation reaction. However, the application in industrial scale was hampered on ground of its complex protocol nature which included usage of hazardous chemicals such as pyridine as well as involvement of multiple silylation and acylation reaction schemes [45-50]. In the pursuit of developing an industrially viable as well as cost-effective technique, Stanssens and his co-workers reported fabrication of a  $\beta$ -dihydroxyalkyl amides using anhydrides/dicarboxylic acids and diethanol amine. However, the polycondensation reaction yielded a partially crosslinked product of gel type nature.

In answer to this juggle, in 1996 DSM's coatings research and development team attained a significant leap towards HBPEA synthesis under the able guidance of Van Bethem. They

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used diisopropanol amine instead of diethanol amine which aided to avoid the gel formation issues by reducing the reactivity rate of the secondary hydroxyl groups of the former reagent [51-54]. Since then, scores of research efforts have been made in order to develop industrially feasible HBPEAs without encountering any issues related to the gelation of the polymeric material.

Concurrently, researchers have been actively pursuing environmentally friendly methods for synthesizing polymers. This includes the development of solvent-free polymerization processes and the utilization of eco-friendly solvents. Starting in the early 1970s, numerous patents and research efforts focused on the synthesis of solvent-free polymer systems, followed by investigations into water-dispersible polymer synthesis, aimed at eco-friendly production of polymers. From 1997 onwards, the concept of waterborne polyester systems emerged as an alternative to solvent-based polymers in general. These waterborne polyesters not only reduce VOC emissions but also offer advantages such as easy to clean, non-toxic, and bear low viscosity. For example, Jung et al. developed UV-curable waterborne unsaturated poly(ester amide) for wood coatings, while Asif and Shi in 2003 synthesized a waterborne polymer system using a polyhydroxy-aliphatic polyester core, Boltorn™ H20, under UV irradiation [55, 56].

In response to the demand for advanced applications and the need to overcome limitations of conventional polymers, the field of intensive polymer research shifted toward nanotechnology, leading to the development of different polymer nanocomposites. These nanocomposites brought about significant improvements in the properties of conventional polyesters, even at very low levels of nanomaterial loading. The concept of polymer nanocomposites emerged in the 1980s, initially proposed by Theng in 1970 [57]. In 1988, Toyota Central Research Laboratories established the first nanoclay-based nylon-6 nanocomposites designed for belt covers, showcasing advanced thermal as well as mechanical properties [58]. There have been innumerable reports on poly(ester amide) nanocomposites incorporating various nanomaterials to enhance properties such as mechanical strength, thermal stability, chemical resistance, and electrical conductivity. For example, Knormann et al. synthesized an unsaturated polyester/montmorillonite nanocomposite in 1998, demonstrating improved fracture energy, and this work was followed by similar studies [58, 59]. Researchers also explored the use of different fibers like carbon, jute, and banana to reinforce polymer composites, thereby enhancing their

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inherent properties [60-62]. Additionally, inorganic nanomaterial-based polyester nanocomposites have been developed to improve the existing properties of polyesters and introduce novel properties for various applications [63, 65].

In summary, the field of poly(ester amide) nanocomposites offers ample opportunities for further exploration, with the potential for advanced applications and improved materials.

### **1.3. Materials and methods**

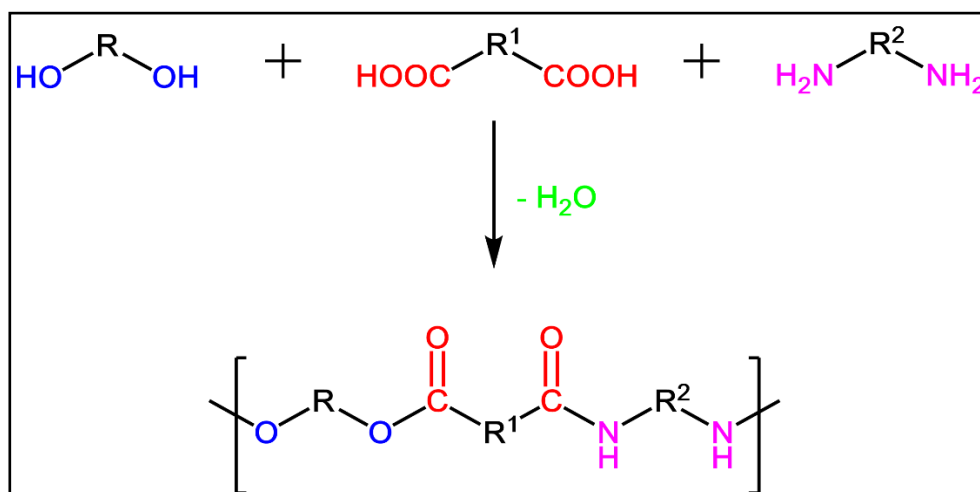
#### **1.3.1. Materials**

In order to accomplish the advanced applications of poly(ester amide)s, it becomes a cardinal task to tailor the polymeric architecture with well-suited building blocks. However, it becomes pertinent enough to address the environmental issues and carry out promotion of the notion of sustainability by invoking the usage of renewable resources as the main precursors bearing intrinsic traits for carrying out synthesis of the polymeric material. In turn, research enthusiasts have also propagated the idea of incorporating nanomaterials into the main polymer framework on the ground of enhancing their inherent properties as well as to extend their applicability genre [53]. As a result, the overall fabrication as well as the collective performance traits of the polymer nanocomposites are dictated by the confluence of various parameters, viz., judicious selection of monomers which are renewable in nature, integration of nanomaterials into the polymer matrices followed by selection of the optimal composition of the nanocomposite [35, 36]. Therefore, this section demonstrates an overarching conclusion of the various monomers and the preparative techniques employed for conducting the fabrication of poly(ester amide) material and their subsequent nanocomposites. However, the main emphasis on discussion of nanomaterials is exclusively confined to biochar material and its modified form. This limitation is on account of the overriding focus of the current thesis on this specified nanomaterial. Nevertheless, a short section on the carbon as well as non-carbon-based nanomaterials will be illustrated with a brief explanation.

##### **1.3.1.1. Poly(ester amide)**

Poly(ester amide)s are considered as an important subclass of polymers which are characterized by the presence of both ester and amide linkages within the polymeric framework. They are known to blend the prominent properties of both polyamides and polyesters. They are primarily synthesized via polycondensation reaction which involve

reaction between amines, carboxylic acids, and polyhydric alcohols under controlled pressure and temperature conditions as illustrated in **Scheme 1.1**. Diols and diacids are generally chosen for preparing the polyester segments wherein diamines are incorporated to introduce the amide units. At times, in order to facilitate controlling of the chain length of the polymer framework, terminal group modification is carried out by introducing monobasic acids such as lactic acid, acrylic acid, etc. [42]. As discussed earlier, most of the precursors are primarily derived from conventional resources, viz., petroleum reserves, etc. However, in response to the escalating trend of procuring environmental consciousness, usage of biogenic resources has received tremendous limelight over the current years [40]. In this juncture, **Table 1.1**, **Table 1.2** and **Table 1.3** provide a catalogue of available di or polybasic carboxylic acids, amines and di or polyhydric alcohols utilized for carrying out synthesis of poly(ester amide)s.



**Scheme 1.1.** Formation of poly(ester amide) by a polycondensation reaction.

Moreover, waterborne poly(ester amide)s are generated from bio based monomers which possess polar functional groups, viz., hydroxyl (-OH) and carboxylic acid (-COOH). The presence of these groups on the periphery of the polymer surface is responsible for conferring water solubility attribute in them. In the current thesis work, glycerol, citric acid, and hexamethylene diamine are utilized as the prime reactants and the presence of -OH and -COOH functional groups on the polymer surface even after its preparation render water solubility as well as waterborne features to the prepared poly(ester amide) resin.

#### (a) Carboxylic acids

The most readily available di or polybasic acids which are biogenic in nature are acquired

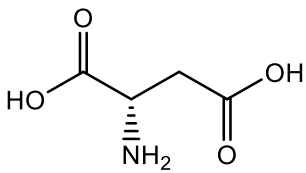
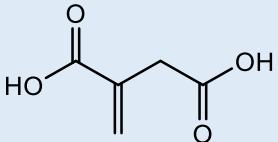
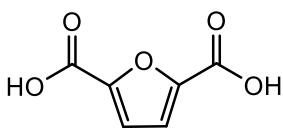
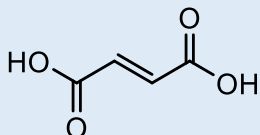
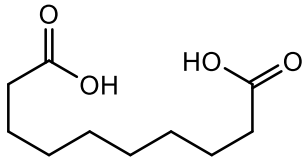
from biomass origins, and a list of them is explicitly detailed in **Table 1.1**. Amongst them, citric acid is considered as one of the most common naturally occurring carboxylic acids which is found exclusively in citrus fruits. It bears one tertiary carboxylic acid group coupled with two primary carboxylic acid functional units. The presence of these reactive linkages facilitate reactions with polyhydric alcohols in order to create a three-dimensional structural entity of poly(ester amide) [66, 67]. Notably, it was observed that citric acid can also behave as a self-catalyst in conducting polycondensation reactions and can aid in enhancing the functional value within the poly(ester amide) framework. Additionally, this trait of citric acid expedites hydrogen bonding interactions along with conferring water borne characteristic to the entire material. Under this context, it can be stated that poly(ester amide)s based on citric acid are known for their good compatibility feature as well as cost effective nature [68]. Another frequently used carboxylic acid which is bio-based in nature is tartaric acid. It is mostly found in fruits, especially grapes and bananas and possesses two secondary hydroxyl functional groups which aid in creating compatibility between the polymeric phases [69, 70]. Succinic acid, found abundantly in broccoli, sugar beets, etc. is also acquired from fermentation process of carbohydrates, viz., sucrose, fructose, glucose or maltose using an anaerobic, Gram negative, bacterial strain known as *Anaerobiospirillum succiniproducens*. In addition, another prominent acid, known as adipic acid, is procured extensively from beet root juices [71]. The presence of two carboxylic acid functional units in both these acids render water solubility along with biodegradability trait to poly(ester amide) material. In recent times, itaconic acid has gained ultimate momentum as a monomer. This carboxylic acid is basically procured via carbohydrate fermentation in the presence of a fungus named, *Aspergillus terreus*, present widely in soil environment [72-75]. The availability of  $\alpha$ ,  $\beta$ -unsaturated bonds in the framework makes it a prospective building block for carrying out synthesis of poly(ester amide) material. Moreover, the existence of this unique functionality bestows tunable features such as shape memory as well as UV-curability to the polymeric material. In addition, itaconic-acid derived poly(ester amide)s can serve as viable substitutes to different acrylated poly(ester amide)s, provided their structural resemblance factor remains close to acrylic acid [76-78]. Many amine-derived dicarboxylic acids, viz., aspartic acid and glutamic acid which are renewable in nature have been extensively utilized in biomedical spheres owing to their versatile unique properties, viz., biodegradability as well as biocompatibility. In contemporary times,

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aromatic acids which are biogenic in nature sketch another valuable category of precursors for synthesis of poly(ester amide)s. They are known to set forth increment in thermal and mechanical properties on the ground of their rigid structural unit. In turn, the aromaticity trait present in this monomer renders distinctive characteristics to the polymeric material. A notable example is 2,5-furandicarboxylic acid which is procured from different carbohydrates sources and their derivatives [80]. The aromatic structure present in it is widely explored and consequently, it is utilized extensively as a bio-based diacid precursor. Moreover, its structural congruity to terephthalic acid makes it a feasible substitute in conducting poly(ester amide) synthesis [81].

**Table 1.1.** Different carboxylic acids with their structure and applications

Name	Structure	Applications
<b>Citric acid</b>		Biomedical domains, tissue engineering scaffolds, biocompatible and biodegradable materials
<b>Tartaric acid</b>		Biodegradable substances
<b>Succinic acid</b>		Biodegradable materials, powder coating formulations
<b>Adipic acid</b>		Pharmaceutical sectors and pesticide, antimicrobial substances
<b>Glutamic acid</b>		Biomedical utilities inclusive of controlled drug delivery and tissue engineering

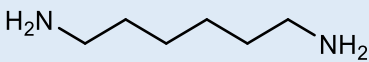
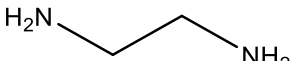
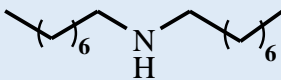
<b>Aspartic acid</b>		Drug delivery utilities
<b>Itaconic acid</b>		UV curable substances, shape memory materials
<b>2,5-Furan dicarboxylic acid</b>		Mechanically tough and biodegradable substances
<b>Fumaric acid</b>		Biomedical uses
<b>Sebacic acid</b>		Hydrophobic, highly flexible, biodegradable and biocompatible materials

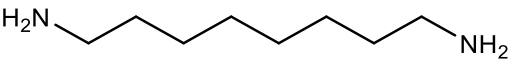
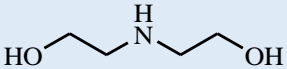
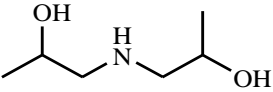
**(b) Amines**

Amines are known to portray a crucial role in the preparation of poly(ester amide)s. Some of the amines which are utilized in carrying out synthesis of poly(ester amide)s, both linear and hyperbranched, are categorically listed in **Table 1.2**. Such commonly used diamines are hexamethylenediamine, ethylenediamine, dioctyl amine, etc. which are further strategically chosen with the purpose of tuning the properties of poly(ester amide) materials. Hexamethylene diamine is regarded as a linear diamine having a long hydrocarbon chain bearing six carbon atoms as well as two amino groups. This diamine incorporated poly(ester amide) is known to possess moderate flexibility as well as good mechanical features [82]. They are commonly used in textiles, automobiles, and as packaging materials. On the other side, ethylenediamine is regarded as another simple yet

important precursor in carrying out the synthesis of poly(ester amide). It is known as a linear diamine entity possessing two amino groups which remain well separated by an ethylene linker moiety. Such diamine based poly(ester amide)s are used widely as packaging materials, coating formulations, and medical devices on ground of their excellent flexibility due to their shorter length of the chain structure [83, 84]. Another prominent amine utilized in the preparation of poly(ester amide) is sebacic diamine. It is primarily derived from sebacic acid and is generally used to render low temperature and flexibility attributes to poly(ester amide)s. It is used extensively as wire insulation materials, elastomers as well as cold-resistant adhesives. Additionally, it has been observed that dihydroxyalkyl amines, viz., diethanol amine and diisopropanol amine are used solely for conducting synthesis of hyperbranched architecture of poly(ester amide)s. In turn, the end groups are tuned using amines such as dioctyl amine, morpholine, diallyl amine, etc. and these amines also execute the role of chain stoppers while carrying out propagation of the hyperbranched chains of poly(ester amide) materials [85]. Therefore, the combination of diisopropanol amine and diethanol amine serve as important precursors for tailoring the functional groups present on the periphery and the molecular weight of the polymer network [82].

**Table 1.2.** Different amines with their structure and applications

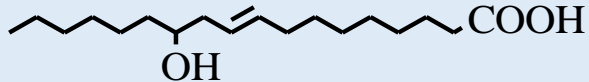


Name	Structure	Applications
<b>Hexamethylene diamine</b>		Automobiles, textiles and packaging materials
<b>Ethylene diamine</b>		Medical devices and coating formulations
<b>Dioctyl amine</b>		Surfactant, softener and anti-static agent

<b>Sebacic diamine</b>		Elastomers, cold-resistant adhesives
<b>Diethanol amine</b>		Corrosion inhibitor, surfactant, and coating formulations
<b>Isopropanol amine</b>		Surfactant, metalworking fluids, wetting agents, etc.

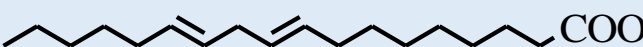
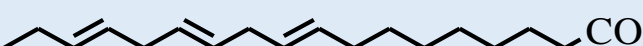


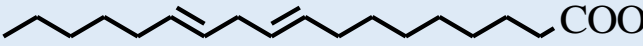
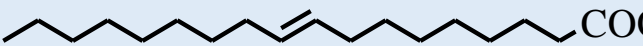
**(c) Vegetable oils**

Vegetable oils inclusive of drying, semi-drying and non-drying oils are utilized for carrying out synthesis of poly(ester amide)s which are bio-based in nature. These oils basically constitute about 94-96% of fatty acid components of the total weight proportion. Various vegetable oils with their distinctive physical properties and their primary fatty acid content inclusive of their structure are listed explicitly in **Table 1.3**.

**Table 1.3.** Various vegetable oils and their major fatty acid profiles

Vegetable oil	Primary fatty acids/ structure	Fatty acid proportion (% of total)	Iodine value
<b>Castor oil</b>	Ricinoleic acid 	90-92	80-88
<b>Soyabean oil</b>	Linoleic acid 	55	125-140
	Oleic acid 	28	



<b>Linseed oil</b>	Linoleic acid 	35	175-204
	Linolenic acid 	40	
<b>Mesua ferrea L.</b>	Stearic acid 	14	89-93
	Oleic acid 	55	
<b>Cottonseed oil</b>	Linoleic acid 	42-52	103-116
	Oleic acid 	18-24	

Amongst the presence of all other non-edible vegetable oils, castor oil serves as one of the most promising feedstocks bearing all the requisite traits inclusive of the presence of exceptionally high proportion of ricinoleic acid as well as a satisfactory shelf life in comparison to other prospective vegetable oils [86-89]. The presence of more than 90-95% of only one fatty acid content considers the oil as a pure chemical. The very fact that India stands as the leading producer of castor oil counts in the exploration of appropriate bioresource for conducting the synthesis of poly(ester amide). Other vegetable oils, viz., soyabean oil, linseed oil, cottonseed oil, etc. and their derivatives primarily N,N-bis(2-hydroxyethyl) fatty amides have gained momentum over the years as an attractive starting material on ground of their good functional reactivity and diluents property [90-93].

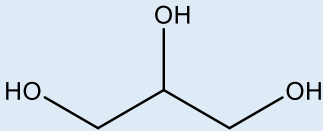
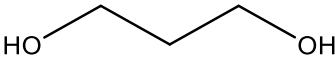
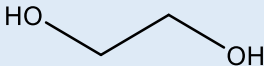
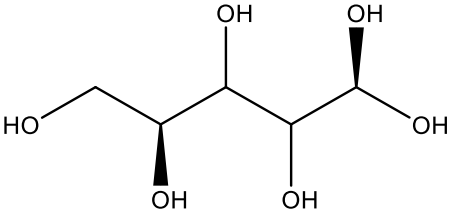
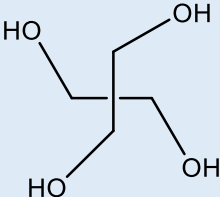
**(d) Polyols**

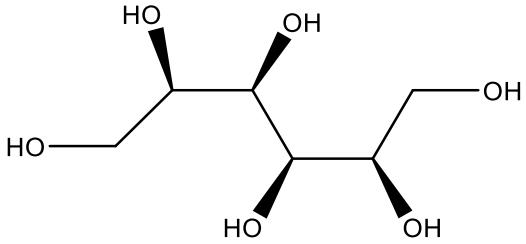
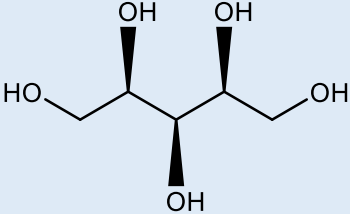
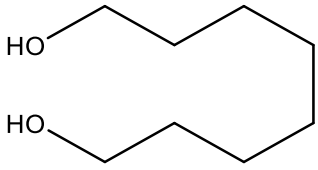
Bio-based polyols/diols delineate an important category of reactants in conducting the synthesis of poly(ester amide)s. **Table 1.4.** demonstrates an overview on some of the keynote examples of diols/polyols. The physicochemical traits of the resulting poly(ester amide) tend to be heavily dependent on a variety of parameters, viz., critical choice of the diols/polyols, etc. Glycerol is regarded as a widely used bio-based solvent (trivalent alcohol) which is derived primarily from the hydrolysis of triglycerides found exclusively in animals and plants sources. The presence of three hydroxyl groups facilitate the formation of branched architecture of poly(ester amide)s, thereby propounding biodegradability and biocompatibility attributes. This versatile nature has led to its usage in diverse biomedical genres [94-96]. Another important bio-based polyol which holds a lot of significance is 1,3-propanediol which is easily accessible from bioconversion of glycerol. Poly(ester amide)s acquired from it display exceptional flexibility, biodegradability, and impact resistance. Ethylene glycol is regarded as another important precursor for conducting poly(ester amide) synthesis. Subsequently, other bio-based polyols, viz., mannitol, pentaerythritol, sorbitol, and xylitol which are derived from sugars, have also attained prominence in carrying out production of poly(ester amide) material [97, 98]. D-mannitol is another significant polyol used to carry out production of poly(ester amide) coupled with biodegradability trait, suitable for utility in a wide range of engineering applications. Sorbitol, another sugar derivative, is being derived from glucose via hydrogenation process. It is commonly used as a building block for carrying out poly(ester amide) synthesis due to the persistence of multiple functional groups, which result in creation of polymeric materials with randomly cross-linked three dimensional networked entities [99]. Consequently, this aid in reinforcing their thermal as well as mechanical properties. Isosorbide has also accumulated attraction in poly(ester amide) synthesis on ground of its robust structure and different functional attributes. This aids in producing high end performing materials that help in resisting UV radiation, chemical exposure, abrasion and heat along with maintaining the biocompatibility feature. 1,8-octanediol and xylitol are also employed as important precursors on account of their availability from renewable sources as well as their non-toxic nature. 1,3-Octanediol is obtained from fermented foods and has great solubility in water wherein xylitol is sourced from fibrous materials and easily dissolves in water [100, 101]. Additionally, pentaerythritol is regarded as a valuable candidate for conducting poly(ester amide)

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synthesis, thereby offering greater photostability in comparison to glycerol. In turn, it is also known to contribute towards the fabrication of poly(ester amide) material that acts as an excellent adhesive via formation of hydrogen linkages with various polar functional groups present on the surface [35, 36].

**Table 1.4.** Different polyols with their structure and applications

Name	Structure	Applications
<b>Glycerol</b>		Biomedical applications, Biocompatible and biodegradable
<b>1,3-Propane diol</b>		Biodegradable material
<b>Ethylene glycol</b>		Biodegradable material
<b>D-mannitol</b>		Biodegradable material, Tissue engineering applications
<b>Pentaerythritol</b>		Biodegradable material, Surface coatings

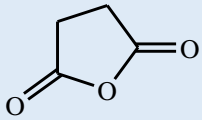
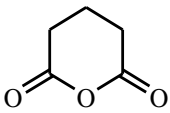
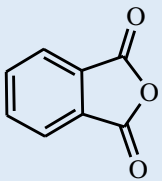
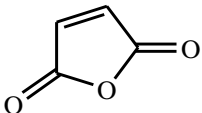
<b>Sorbitol</b>		Biodegradable material
<b>Xylitol</b>		Biocompatible material, Tissue engineering as well as drug delivery agent
<b>1,8-Octane diol</b>		Biocompatible and biodegradable material

**(e) Anhydrides**

Anhydrides portray a significant role in carrying forth poly(ester amide) synthesis as one of the core components used in the reaction to facilitate the formation of the polymeric material. At times, they can also be utilized as crosslinking agents, while conducting the poly(ester amide) synthesis. The anhydride is usually added into the reaction mixture after the prepolymer formation. Following that, the anhydride generally carries out a ring opening polymerization reaction with the carboxyl groups present on the polymeric surface yielding amide functionalities along with release of cyclic anhydride as byproducts [33, 34]. The anhydrides can also play the role of crosslinking agents, which aid in increment of the thermal and mechanical parameters by forming additional bonds with the polymer chains. They have found prospective utilities in various fields as coating formulations, adhesives, etc. These anhydrides are primarily opted based on the lucrative traits of the polymer material, viz., adhesion, chemical resistance, flame retardancy, etc. [102, 107]. This further permits for precise customization of the poly(ester amide) material to meet different application requirements. **Table 1.5.** provides a list of various anhydrides

used in carrying out synthesis of poly(ester amide) material along with their structure and applications.

**Table 1.5.** Different anhydrides with their structure and applications

Name	Structure	Applications
<b>Succinic anhydride</b>		Coating formulations
<b>Glutaric anhydride</b>		Coating binders
<b>Phthalic anhydride</b>		Adhesives, coating materials
<b>Maleic anhydride</b>		Flame retardants, coating formulations

**(f) Catalyst**

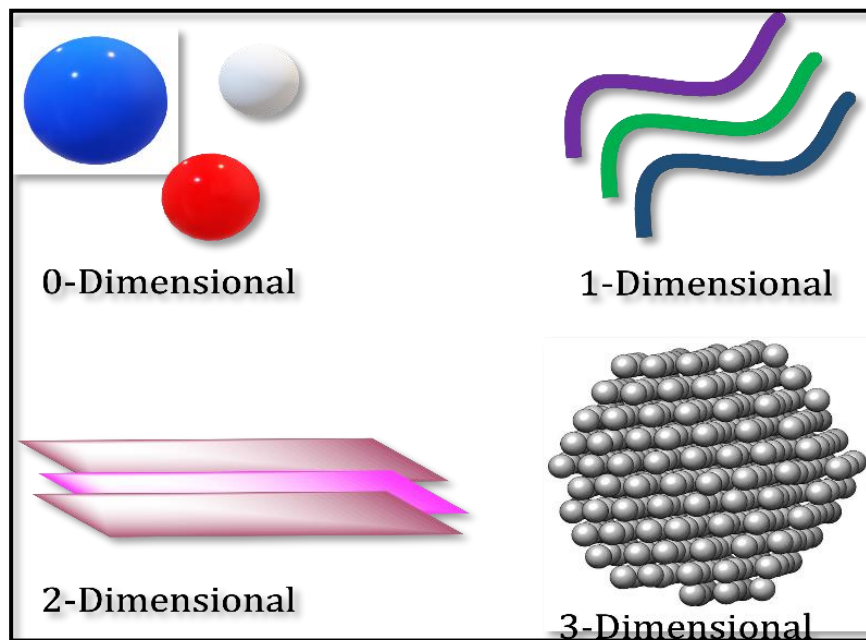
Catalysts portray a pivotal role in carrying out acceleration of the polycondensation reactions which are integral to poly(ester amide) synthesis. This stands out to be applicable especially at the industrial scale, wherein lengthy time regime for conducting the reaction would project out to be highly impractical in nature. Different types of catalysts, viz., bases, acids, coordinated complexes and metals have been documented in literature for facilitating poly(ester amide) synthesis. Under this context, many inorganic acids like sulfuric and phosphoric acids have found their utility in conducting catalysis of aliphatic poly(ester amide) resin under exposure to mild reaction conditions [108, 109]. Many catalysts, especially triflate catalysts which are solely derived from rare earth metals, viz.,

zinc, bismuth, etc. have found their efficacy in promoting the polycondensation reactions involving the synthesis of poly(ester amide) resin, subjugation to mild conditions. The catalysts facilitate the conversion of aliphatic diols, acids and amines to their respective end products at shorter reaction tenure as well as lower temperature conditions. Many metal derived catalysts have also been rigorously explored in conducting different poly(ester amide) synthesis routes. Earlier, titanium-based catalysts were extensively used in carrying out reaction, however, concerns about their potential degradation have induced a shift towards usage of germanium as well as zirconium-based catalysts on ground of their robust nature. Over the years, many enzymatic catalysts are also gaining prior traction owing to their environmentally friendly mode of fabrication, specifically in biomedical spheres [112, 113]. However, the shortcoming of enzymatic catalysts lies in their elevated cost levels, which can hamper the overall cost of poly(ester amide) production. Different lipases and hydrolases acquired from *Candida antarctica* have posed as effective catalysts in driving forward manifold polycondensation reactions. In the domain of waterborne poly(ester amide) synthesis, various catalysts stood out as valuable, viz., titanium (IV) n-butoxide, *para*-toluene sulphonic acid, tin chloride, dibutyl tin laurate, etc. These catalysts portray an outstanding role in carrying out controlled and efficient synthesis of poly(ester amide)s for different applications [115].

### **1.3.1.2. Nanomaterial**

Nanomaterials, characterized by their nanoscopic dimensions falling within the range of 1-100 nm, represent the core of a burgeoning technological revolution. They can be of natural or human-made origin; each category possessing distinct properties that set them apart. Nanomaterials have garnered significant attention in the 21<sup>st</sup> century across diverse fields such as electronics, materials science, and biomedical science. This attention is primarily due to their remarkable properties, including mechanical, thermal, electrical, and biological attributes. These nanomaterials play a pivotal role in the fabrication of various polymer nanocomposites. The choice of nanomaterial significantly influences the desired properties, performance characteristics, and applications of nanocomposites. Factors such as size, aspect ratio, surface area, shape, and uniform distribution of nanomaterials within the polymer matrix play a crucial role in enhancing the properties of these nanocomposites [116].

Nanomaterials can be categorized based on their dimensions and origin. Depending on their dimensions, nanomaterials fall into three classes: (i) 0-D, (ii) 1-D, (iii) 2-D and (iv) 3-D materials, as depicted in **Figure 1.1**. These materials exhibit diverse shapes, such as spheres, wires, rods, fibers, ribbons, sheets, tubes, cubes, and more [117].



**Figure 1.1.** Different classes of nanomaterials and 3-D material.

**(a) Carbon-based nanomaterials**

Carbon-based nanomaterials have captured the scientific community's imagination, owing to carbon's unique hybridization and sensitivity properties. The discovery of buckminsterfullerene ( $C_{60}$ ) in 1985, followed by carbon nanotubes (CNTs) in 1991 and graphene in 2004, marked significant milestones in the development of carbon-based nanomaterials. These materials, of organic origin, exhibit exceptional properties, including excellent thermal, mechanical, and electrical characteristics. They can exist in various dimensions, viz., 0-D, 1-D, and 2-D.

Carbon-based nanomaterials, such as graphene sheets and their derivatives (graphene oxide (GO), reduced GO (rGO)), CNTs, cellulose nanofiber (CNF), carbon dot (CD), and nanodiamonds, offer a diverse array of nanostructures. Among them, nanofibers, a 1-D structure, stand out. CNFs are derived from bio-based sources such as trees, plants, algae, marine organisms, and bacteria. CNF, composed of polysaccharides with  $\beta$ -linked D-glucose units in their chemical structure, feature -OH groups in their backbone, facilitating surface functionalization and property enhancement [118-121].

Graphene, a widely used carbon-based nanomaterial, boasts a single layer with a two-dimensional honeycomb crystal structure. The  $sp^2$  bonded carbon atoms impart exceptional properties, including electrical, thermal, biological, and mechanical characteristics. Graphene enhances polymer hosts in nanocomposite fabrication, although achieving uniform dispersion within the polymer matrix, especially in waterborne polymers, can be challenging due to the non-polar nature of graphene sheets. In order to address this challenge, GO has emerged as a solution, as it contains oxygenated functional groups, rendering it polar in nature. GO, with functional moieties like epoxide, hydroxyl, carboxylic, carbonyl, phenol, lactone, and quinone, presents excellent properties for various applications, including photocatalysis, supercapacitors, hydrogen storage, sensors, and solar cells.

Another noteworthy 2-D carbon-based nanomaterial is graphitic carbon-nitride ( $g-C_3N_4$ ), created by modifying graphene sheets through nitrogen substitution.  $g-C_3N_4$  features  $sp^2$  hybridized carbon and nitrogen atoms with minimal impurities of hydrogen and oxygen. These nanomaterials are photocatalytic and possess unique surface properties, making them valuable for applications such as energy storage and photocatalysis [122].

Recently, biochar has garnered a lot of speculation as a 0-D based nanomaterial. Biochar exhibits remarkable nanoscale characteristics that make it a compelling subject of interest. Biochar is a carbonaceous material produced through the pyrolysis or thermal decomposition of biomass under controlled conditions. Its intricate porous structure, resembling a sponge at the nanoscale, offers a vast internal surface area and a unique network of tunnels and channels. At the nanoscale, biochar's pores and crevices provide an ideal habitat for microorganisms, enhancing soil fertility and promoting plant growth. This nanomaterial acts as a carbon sink, sequestering carbon in the soil, contributing to climate change mitigation. Biochar's application extends beyond agriculture; its high porosity and large surface area make it an excellent candidate for water purification. The 3-D nature of biochar facilitates the adsorption of pollutants, heavy metals, and organic contaminants from water, rendering it a sustainable solution for water treatment [123, 124].

In summary, biochar's exceptional 0-D nanostructure, with its myriad of pores and tunnels, underpins its multifaceted utility. Its role in agriculture, carbon sequestration, and water purification showcases the versatility of this nanomaterial, addressing critical challenges in sustainable agriculture and environmental management.

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***(b) Non-carbon-based nanomaterials***

Non-carbon-based nanomaterials, inorganic materials with nanoscale dimensions, can be obtained naturally or synthetically from various inorganic precursors. These materials, available in dimensions ranging from 0-D to 2-D and exhibiting shapes like spheres, rods, cubes, wires, sheets, layers, etc., include naturally occurring nanoclays, silicates, minerals, as well as synthetically engineered nanosized metals, metal oxides, sulfides, chalcogenides, phosphates, fluorides, and chlorides [125]. For instance, metal-based nanomaterials are typically produced by reducing metal precursors with the aid of capping agents, allowing for control over their morphologies and sizes. These inorganic nanomaterials offer excellent electronic, optical, magnetic, catalytic, and other properties. Natural inorganic nanomaterials feature exceptional surface properties and biocompatibility, further enhancing their utility across a range of applications [126].

***(c) Hybrid nanomaterials***

Hybrid nanomaterials are synthetic materials composed of two or more distinct nanomaterial types, linked through covalent or non-covalent interactions. These hybrids often involve a combination of carbon-based and inorganic nanomaterials, leveraging the unique properties of each component to create a synergistic effect within the hybrid structure. Hybrid nanomaterials are versatile and can be classified into categories like carbon-carbon, metal-metal, and metal-carbon nanohybrids [127]. These materials offer exceptional properties, such as catalytic, optical, electronic, sensing, and energy storage capabilities, within a single nanostructure. Their properties can be tailored and enhanced by adjusting the composition and components of the hybrid, making them valuable materials for various applications.

In summary, nanomaterials are at the forefront of scientific and technological advancements, with diverse classes and origins that open up a world of possibilities for innovative applications in fields ranging from electronics to biomedicine. Their unique properties and tunability make them indispensable in the development of advanced materials and nanocomposites [128].

**1.3.2. Methods**

**1.3.2.1. Preparation of poly(ester amide)s**

The conventional synthesis of poly(ester amide)s typically involves polycondensation

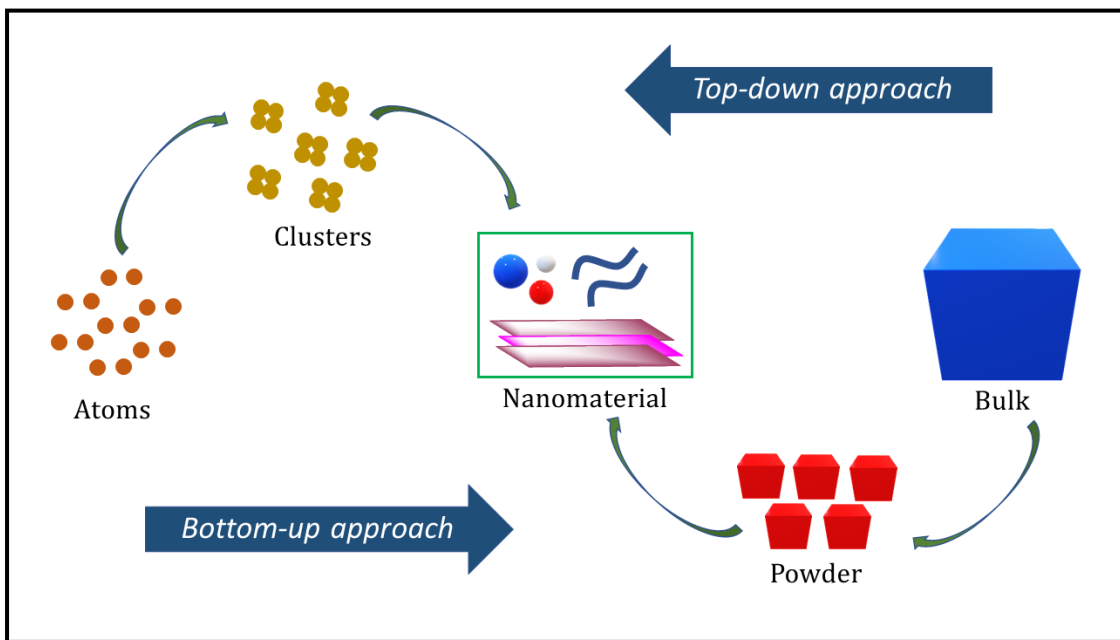
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reactions between diacids, diols and amines at elevated temperatures, with the elimination of water as a by-product. This synthetic route often requires the use of a catalyst, which can either be an external catalyst or a diacid monomer that acts as a self-catalyst. Various methods can be employed for poly(ester amide) synthesis, but the most commonly used ones are step-growth polymerization, ring-opening polymerization, and polyaddition reactions. Step-growth polymerization involves the reaction of dicarboxylic acids or their functional derivatives with diols or their derivatives, followed by amines which further result in carrying out elimination of water or methanol as a by-product, depending on the reactants used. Metal-based catalysts, such as titanium, aluminum, antimony, and germanium compounds, are commonly employed in this method. Titanium and antimony-based catalysts are particularly popular due to their lower residual catalyst content. However, this type of polymerization often requires a lengthy reaction time span, although it can be expedited by adjusting the reaction conditions, such as using higher temperatures and vigorous mechanical stirring. Ring-opening polymerization is another innovative method for synthesizing poly(ester amide)s, where cyclic monomers are utilized to produce high molecular weight linear poly(ester amide)s. This process necessitates the use of a catalyst or initiator [129, 130]. The advantages of ring-opening polymerization include the ability to obtain high molecular weight poly(ester amide)s under mild conditions without formation of the by-products. Additionally, various techniques like resin transfer molding, pultrusion, and melt filtration can be applied in this method. Polyaddition reactions involve the reaction of diisocyanates with diacids or anhydrides of dicarboxylic acids and diols, catalyzed by different catalysts like ammonium salts, amines, and metal-based catalysts. However, this method possesses the drawback of potential side reactions, limiting its usage in poly(ester amide) synthesis.

Different synthetic procedures for poly(ester amide)s employ various solvents, which can lead to the emission of VOCs into the atmosphere, causing environmental pollution. To address this concern, the use of water as a solvent has gained cardinal attention, leading to the development of waterborne poly(ester amide)s. In these waterborne poly(ester amide)s, the polymeric chains typically contain carboxylic acid, amines, and hydroxyl groups that ionize and form salts when strong alkalis or bases, such as triethylamine, are used. The number of terminated hydroxyl and carboxylic acid groups in the polymeric chains influences the water dispersion stability. Several reports are available on the synthesis of waterborne poly(ester amide)s [131].

### 1.3.2.2. Nanomaterial preparation

The preparation of nanomaterials can generally be categorized into two approaches, viz., the "top-down" approach and the "bottom-up" approach as illustrated in **Figure 1.2**. The "top-down" approach involves the reduction of bulk materials into smaller particles through techniques like ball-milling, laser ablation, mechano-chemical processes, and electrochemical methods. Conversely, the "bottom-up" approach entails the assembly of nanoscale structures from atomic or molecular precursors, often involving processes such as pyrolysis, condensation, and polymerization [132].



**Figure 1.2.** Preparative approaches of nanomaterials.

These approaches further lead to the synthesis of nanomaterials through three major methods: (a) biological methods, (b) physical methods, and (c) chemical methods.

#### **(a) Biological methods**

Biological methods offer an eco-friendly approach to nanomaterial synthesis, involving microorganisms such as bacteria, fungi, and algae. These microorganisms can be employed to synthesize nanomaterials from aqueous solutions of metal salts. For instance, magnetotactic bacteria found in the depths of the sea create magnetosomes containing nanosized magnetic iron oxide nanocrystals ( $\text{Fe}_3\text{O}_4$ ) and magnetic iron sulfide ( $\text{Fe}_3\text{S}_4$ ) through a biomineralization process, which they use for geomagnetic navigation. Other microorganisms like *Pseudomonas cells* and *Rhodopseudomonas capsulata* can

biosynthesize palladium and gold nanoparticles, while fungi like *Fusarium oxysporum* are used to synthesize silver nanoparticles. Algae, such as *Sargassum wightii*, have also been employed for the extracellular synthesis of gold nanoparticles. However, the use of certain pathogenic microorganisms is limited in these processes. Additionally, plants extracts containing phytochemicals can serve as reducing agents for the synthesis of various metal nanoparticles like gold, silver, zinc, cobalt, copper, and nickel, each with distinct sizes and shapes [133-135].

**(b) Physical methods**

Physical methods for nanomaterial synthesis include mechanical attrition, melt mixing, and evaporation-based techniques. Mechanical attrition involves grinding macro- or micro-sized particles into smaller ones using various milling methods. Melt mixing, on the other hand, combines molten streams of metals at high velocities to form nanoparticles. Evaporation-based methods, such as laser ablation and laser pyrolysis, involve the conversion of materials into a gaseous phase followed by cluster formation and deposition on suitable surfaces [136]. These methods are typically conducted in vacuum chambers to prevent oxidation of materials and ensure product purity.

**(c) Chemical methods**

Chemical methods for nanoparticle synthesis primarily follow the bottom-up approach, utilizing liquid or gaseous phases. These methods offer the advantage of precise control over particle size and shape. Common chemical methods include co-precipitation, sol-gel, hydrothermal/solvothermal techniques, sonochemical, and microwave-assisted methods [137].

*Co-precipitation:* In this method, water-soluble metal salts are mixed, leading to the formation of water-insoluble salts, followed by precipitation. Reducing agents like liquid ammonia and sodium hydroxide maintain an alkaline pH, and heat can be applied to enhance crystallinity [138].

*Sol-gel:* This method involves the hydrolysis of metal alkoxides, followed by polycondensation in the presence of acid or base. This method subsequently results in the formation of a gel, which eventually transforms into a powder [139].

*Hydrothermal/Solvothermal:* These methods utilize high pressure and temperature in aqueous or non-aqueous solvents to promote crystal growth. Control over temperature and time allows for size and shape modulation [140].

*Sonochemical:* Ultrasonic irradiation in a liquid medium creates transient hot zones, leading to the formation of nanoparticles by breaking down precursors [141].

*Microwave-assisted:* Electromagnetic energy is converted into thermal energy to heat precursors, reducing the synthesis time [142].

### **1.3.2.3. Fabrication of polymer nanocomposites**

Polymer nanocomposites, which involve incorporating nanomaterials into polymer matrices, have emerged to meet the demand for high-performance polymers. Several techniques are employed for fabricating polyester nanocomposites, with the most common methods being solution mixing (ex-situ), in-situ polymerization, and melt mixing.

#### ***(a) Solution mixing (Ex-situ) technique***

Solution mixing (ex-situ) involves a solvent-based approach where the solvent should effectively solubilize and disperse both the poly(ester amide) resin and nanomaterials. Initially, nanomaterials are swollen and dispersed in a suitable solvent through mechanical force and ultrasonication. The resulting nanomaterial solution is mixed with a prepolymer or poly(ester amide) solution, followed by agitation using methods such as ultrasonication, magnetic stirring, or shear mixing. Evaporation of the solvent then yields the poly(ester amide) nanocomposite. Effective agitation is crucial to disintegrate nanomaterial agglomerates, ensuring uniform dispersion. The interaction between poly(ester amide), nanomaterials, and solvent governs nanocomposite fabrication. Strong poly(ester amide)-nanomaterial interaction results in nanocomposite formation, while strong poly(ester amide)-solvent interaction leads to agglomerated nanocomposites [150, 141]. Dominant nanomaterial-solvent interactions prevent nanocomposite formation.

#### ***(b) In-situ technique***

The in-situ technique involves adding nanomaterials to monomers or prepolymers at the outset, followed by a single-step polymerization reaction to produce the nanocomposite. Monomers or prepolymers, due to their lower viscosity compared to polymers, facilitate nanomaterial dispersal and prevent agglomeration during polymerization. The continuous

mechanical agitation prevents nanomaterial agglomeration, resulting in a homogeneous nanocomposite [136, 140]. This technique is often preferred for fabricating poly(ester amide) nanocomposites.

*(c) Melt-mixing technique*

Melt mixing is commonly used for thermoplastic polymer nanocomposites. In this technique, molten polymer is directly mixed with a predetermined amount of nanomaterial through processes such as extrusion molding, injection molding, or compression molding. The polymer is heated to its melting or glass transition temperature [134].

**1.4. Characterization**

A brief comprehensive analysis of the prepared poly(ester amide)s, the carbon-based nanomaterials, nanohybrids and the corresponding poly(ester amide) nanocomposites reckons on the usage of a wide variety of spectroscopic, diffraction and microscopic techniques in order to scrutinize the physicochemical behavior of these synthesized materials. This section depicts a concise overview of the characterization methods in detail.

**1.4.1. Spectroscopic techniques**

**1.4.1.1. Fourier transform infrared (FTIR) spectroscopy**

Fourier transform infrared (FTIR) spectroscopy is considered as a foundational spectroscopic tool to assess the presence of specific chemical linkages as well as functional groups within the prepared poly(ester amide) framework and its respective nanocomposites. In this methodology, molecules of the sample under speculation undergo vibrational changes upon absorbing the infrared ray of the electromagnetic spectrum. The functional groups of interest, viz., hydroxyl (-OH) groups, carbonyl (-C=O) functional groups, amine (-NH) groups, aromatic and aliphatic C=C bonds, alkoxy (-C-O) groups exhibit prominent IR absorption peaks within the IR wavelength ambit of 400-4000  $\text{cm}^{-1}$ . In the case of poly(ester amide)s, a distinct IR absorption peak for carbonyl functional group which corresponds to ester linkages lies in the IR stretching frequency of approximately 1700-1740  $\text{cm}^{-1}$ . In turn, other potential functional groups present in the poly(ester amide) materials include hydroxyl (-OH) groups, -NH bonds of amines and amides, carbonyl functional groups present in amide linkages, and -C-O functional groups

in alkoxy units. The distinct stretching frequencies of these groups are observed at 3200-3400  $\text{cm}^{-1}$ , 3400-3500  $\text{cm}^{-1}$ , 1630-1700  $\text{cm}^{-1}$ , and 1060  $\text{cm}^{-1}$ , respectively. Therefore, it can be stated that FTIR spectroscopy is an important yardstick and is valuable in carrying out confirmation regarding the formation of various polymers, nanomaterials and their corresponding nanocomposites [135, 136]. It also serves as a preliminary step to confirm their fabrication via characterization. In addition, assessments of various molecular interactions, viz., the extent of hydrogen bonding occurring within the polymeric framework, or the nanocomposite can be properly examined by studying the shifts in FTIR bands.

#### 1.4.1.2. Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy is regarded as a valuable analytical method that delves into the magnetic features of atoms, thereby aiding in structural elucidation by carrying out assessments of the prominent chemical environments surrounding the atomic nuclei. Typically, carbon ( $^{13}\text{C}$ ) and proton ( $^1\text{H}$ ) NMR spectra are engaged to discern different types of carbon (C) and hydrogen (H) atoms existing within various organic molecules. Additionally, NMR spectroscopy proves instrumental in assessing various aspects, viz., stereochemistry, isomerism, yield, degree of branching (DB), and different polymerization kinetics revolving organic compounds, other than providing valuable insights into the chemical structures. The degree of branching (DB) parameter holds an important significance in elucidating structural characterization of polymers, thereby providing useful insights into the branching patterns existing within the polymeric chains. It is primarily quantified using the Frechet's equation, which represents the ratio of the sum of the integration values of both terminal (T) as well as dendritic (D) entities to the sum of the total integration values of T, D as well as linear (L) units. A DB value of 0 signifies linear polymers whereas a DB value of 0.5 and 1 represents hyperbranched polymers and dendritic polymers, respectively; although literature at times, considers DB values in the range of 0.5-0.9 for hyperbranched polymers. Moreover, this characterization technique proves invaluable in assessing different organic functional groups which are present in the nanomaterials. Specialized NMR techniques, viz.,  $^{29}\text{Si}$ ,  $^{19}\text{F}$ ,  $^{15}\text{N}$ , and  $^{31}\text{P}$ -NMR are considered as essential tools for conducting characterization of nanomaterials bearing such elements [137].

### **1.4.1.3. Raman spectroscopy**

Raman scattering is noted as a powerful analytical tool employed in order to investigate the rotational characteristics, vibrational modes, and other low-frequency traits of nanomaterials. This methodology is regarded as a highly sensitive tool towards the orientation as well as crystalline traits of molecules existing within the nanomaterial structures. This method finds significant utility in the characterization of carbon-based nanomaterials, viz., biochar, GO, etc. Under this technique, the nanomaterials are exposed to a laser beam which is a monochromatic source of light in the near infrared (IR) or near ultraviolet (UV) range. Upon undergoing excitation, electrons eventually encounter relaxation followed by emission of photons, which can further result in scattering of photons either elastically (known as Rayleigh scattering) or inelastically (known as either Stokes or anti-Stokes scattering). It is found that carbon-based nanomaterials share some common spectral traits in their Raman spectra, notably the D band at approximately  $1350\text{ cm}^{-1}$  and the G band at around  $1580\text{ cm}^{-1}$ . The D band signifies the presence of disorderliness in the graphitic sheets, whereas the G band indicates the breathing modes of  $sp^2$  hybridized bonds present within the graphitic domains of the material. Under this gamut, the ratio of the intensities of the D band to the G band serves as a gauge of assessing all the structural defects [138]. Herein, higher  $I_D/I_G$  values signify greater unkemptness in the structure of the material. Additionally, Raman spectroscopy is widely utilized to carry out characterization of different metal and metal derived nanomaterials. In turn, this method proves helpful in studying the effect of nanomaterials on the fabrication of polymer nanocomposites, thereby shedding light on the interactions as well as on their structural modifications existing within the polymer and the nanocomposite matrix.

### **1.4.1.4. X-ray photoelectron spectroscopy (XPS)**

XPS is considered as a non-invasive surface analysis methodology that determines the elemental composition present at the surface of the material, provides information about the electronic structure of the chemical groups present on the surface of the material as well as unveils information about the oxidation states of the elements present on the surface of the polymeric material. The basic procedure is inclusive of exposing the sample to an X-ray beam which is mono-energetic in nature, followed by carrying out measurement as well as quantification and calculation of the kinetic energy released by the emitted electrons. This technique is frequently employed to scrutinize the composition



of the elements as well as the chemical bonds present in the nanomaterials. In addition, XPS is capable enough to detect the presence of specific heteroatoms, viz., magnesium (Mg), nickel (Ni), sulfur (S), aluminum (Al), etc. in different nanomaterials as well as nanohybrids. These specific heteroatoms may remain undetected by FTIR analysis alone, thereby highlighting the fact that XPS itself is a pivotal technique for conducting comprehensive analysis [139, 140].

#### **1.4.1.5. Ultraviolet-visible (UV-vis) spectroscopy**

UV-vis spectroscopy is regarded as an initial and fundamental spectroscopic method for carrying out characterization of functional groups in polymers, nanomaterials as well as nanocomposites. Typically, this method is engaged to analyze entities with unsaturation, conjugation, and their ability to absorb UV-visible ray of the electromagnetic spectrum which lies within the range of 200-800 nm. Different functional units display electronic transitions, viz.,  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and charge transfer upon carrying out absorption of UV-visible radiation. This mode of spectroscopy is known to provide basic insightful data on the sizes, agglomeration states, and shapes of various prepared nanomaterials. Under the domain of poly(ester amide) nanocomposites, the existence of different nanomaterials in varying proportions directly affect the intensity, position, and nature of peaks observed in their corresponding UV-vis spectra. In turn, the dispersion state of the prepared nanomaterials existing within the poly(ester amide) matrix is closely associated to the transparency exhibited by the nanocomposites, a trait investigated using this technique. In turn, UV-vis spectroscopy is also employed to track down the progress of the reaction and their kinetics studies. Moreover, the absorbance values obtained from UV-visible spectra are used to assess the bandgap available in nanomaterials as well as nanocomposites. Overall, this versatile methodology finds its extensive utilities in various applications, viz., studying the extent of catalytic reactions, radical scavenging activities, photocatalytic degradation of organic moieties or pollutants, heavy metal sensing, etc.

#### **1.4.1.6. Photoluminescence (PL) spectroscopy**

This is noted as another important optical characterization method employed to speculate the luminescent features of nanomaterials as well as their polymer nanocomposites. This mode of spectroscopy basically deals with the emission bands resulting from either fluorescence or phosphorescence emissions. In addition, this mode of spectroscopy

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enables determination of the quantum yield of a sample, coupled with the usage of UV-vis mode of spectroscopy. In this spectroscopy, quinine sulfate is often used as the reference for conducting the assessment of samples. Certain examples of its applications include recent synthesis of poly(ester amide)s by Zia et al. which is bio-based in nature and also exhibited fluorescence properties (green fluorescence) via zwitterionic copolymerization [141, 142].

## 1.4.2. Diffraction technique

### 1.4.2.1. X-ray diffraction (XRD)

It is regarded as an invaluable non-destructive characterization method which is utilized to evaluate the phase purity and degree of crystallinity in different nanomaterials, nanohybrids and their corresponding polymer nanocomposites. Additionally, this technique helps in investigating the crystal structure and interlayer distance of the nanostructured materials. XRD technique is known to identify the crystal structure of the materials by measuring the angles as well as intensities of the diffraction peaks followed by calculating the interlayer distance invoking the usage of the Bragg's equation which is illustrated below in **Equation 1.1**.

$$n\lambda=2d\sin\theta \quad (1.1)$$

where 'n' represents the order of diffraction, which is usually a positive integer,  $\lambda$  refers to the wavelength of the incident X-ray,  $\theta$  denotes the angle of diffraction, and 'd' refers to the interplanar distance. It is generally observed that an increase in the interlayer distance results in the diffraction peak shifting towards a lower diffraction angle. In this regard, the shifting of diffraction peaks as well as the increase in interlayer distance in polymer nanocomposites reveal the intercalation of polymeric chains within the layers of the nanomaterials, thereby providing insightful knowledge regarding the interactions between the polymer matrix and the nanomaterial [143]. In addition, XRD patterns enable the evaluation of crystallite size using the Scherrer equation which is illustrated below in **Equation 1.2**.

$$L=K\lambda/\beta\cos\theta \quad (1.2)$$

where 'L' denotes the crystallite size,  $\lambda$  refers to the wavelength of the incident X-ray, 'K' represents the shape factor,  $\theta$  denotes the angle of diffraction (Bragg's angle), and  $\beta$  signifies the broadening line at half the maximum intensity after carrying out subtraction of the instrumental broadening.

### **1.4.3. Microscopic techniques**

#### **1.4.3.1. Optical microscopy (OM)**

This mode of microscopy is widely employed as an important technique to magnify the small objects using polarized visible light. It enables capturing of the image using photosensitive cameras which further facilitates a close study of the surface characteristics in polymers, nanomaterials as well as nanocomposites. For instance, Ansari et al. in 2022 conducted research on amino acid based poly(ester amide)s and utilized OM to visualize its surface, thereby revealing a spherulitic granular morphology. In addition, Marcovich et al. evaluated the agglomeration behavior of different cellulose nanocrystals in polyurethane nanocomposites via OM image analysis [145].

#### **1.4.3.2. Scanning electron microscopy (SEM)**

It is regarded as an advanced microscopic technique which is exclusively employed to conduct in-depth investigations into the topography as well as the surface morphology of the nanomaterials and the polymer nanocomposites. Unlike OM, SEM principally operates by scanning through surface of the sample taken under consideration with a focused beam of electrons. In turn, this instrument utilizes electromagnetic lenses to capture the high-resolution micrographs. Moreover, in SEM, an electron beam bearing excessively high energy is projected onto the surface, and the electrons upon interacting with the sample are scattered back and further harnessed for carrying out different imaging purposes. These electrons, emanating from both elastic as well as inelastic scattering, result in interactions between the surface of the sample and the beam of electrons, known as backscattered electrons and secondary electrons, respectively. They are subsequently detected by invoking usage of special detectors such as solid-state detector and Everhart-Thornley detector, respectively. SEM is instrumental not only in perceiving the size and shape of nanomaterials, but also in conducting elucidation of the dispersion patterns of nanomaterials incorporated within the polymer matrix [136, 146].

#### **1.4.3.3. Field emission electron microscopy (FESEM)**

This mode of microscopy signifies an upgraded technique known for its superior resolution factor and quality of images in comparison to conventional SEM technique. The key difference between SEM and FESEM lies in the source of emission; the former mode relies on a heated tungsten filament for ejection of thermal electrons, whereas the later employs a field emission gun to emit the electrons. Additionally, in this mode of microscopy, the ejected electrons possess lower energy, thereby significantly increasing the resolution of the microscopic images of the sample under investigation. This method holds immense significance in carrying out characterization of nanomaterials, nanohybrids and their corresponding polymer nanocomposites., thereby providing room for precise investigation of their surface morphology along with fine structural intricacy details [147].

#### **1.4.3.4. Transmission electron microscopy (TEM)**

This version of microscopy stands out as a crucial microscopy technique, exclusively valuable for carrying out characterization of the nanomaterials, nanohybrids and their polymer nanocomposites. This technique portrays a unique role in assessing not only the morphology, particle size or crystallographic structure of the nanomaterials but also the dispersion state of the nanomaterials persisting within the polymer nanocomposites. In TEM, a high energy electron beam is allowed to transmit through an ultrathin section of the sample under consideration, which further carries out transmission of electrons in order to reveal the internal structure. TEM basically offers two modes of imaging, viz., the dark field mode, where diffracted electrons are utilized for imaging purpose and the bright field mode, which incorporates the usage of only transmitted electrons for imaging purpose. In addition, TEM offers atomic scale information about the interplanar distances existing within the nanostructures, minute details regarding crystallinity of the samples via high resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns, respectively [148]. Moreover, TEM can also aid in evaluating the elemental compositions of the samples when coupled with energy dispersive X-ray (EDX) analysis.

#### **1.4.3.5. Inverted microscopy (IM)**

It is a widely known microscopic method for performing visualization of minutely designed particles, especially biological moieties. It primarily comprises of a light source and condenser lens which are designed to get positioned at the top of the instrument, with

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the objective lens aligned beneath and pointed in the upward direction. This mode of microscopy finds widespread applications in conducting the study of cell morphology as well as investigating the biocompatibility of poly(ester amide) nanocomposites [149]. Thereby, this variant of microscopic technique provides valuable insights into the biological materials and samples existing at the microscale.

#### **1.4.4. Other techniques**

##### **1.4.4.1. Thermogravimetric analysis (TGA)**

TGA stands out as a crucial yardstick for conducting the assessment of thermal stability of polymers, nanomaterials, and their corresponding polymer nanocomposites. The assessment is carried out by monitoring the weight loss as a function of temperature under exposure to different heating rates in an inert atmosphere. This versatile tool extends its utility to scrutinize the degradation kinetics, evaluation of varied processes, viz., adsorption, absorption, desorption, etc., calculation of char residue as well as exploring the phase transitions, amongst other widespread applications. From the TGA data, different attributes can be examined which are inclusive of initial degradation temperature abbreviated as (TON), the maximum degradation temperature and the end-set degradation temperature abbreviated as (TMAX) and (TEND), respectively [150]. In turn, the degradation patterns of the samples under evaluation are deduced from the first derivative thermograms coded as DTG. Moreover, TGA aids in identifying the existence of different volatile substances, plasticizers, and fillers within the samples under investigation, thereby providing comprehensive information about the thermal nature and compositions of the samples.

##### **1.4.4.2. Differential scanning calorimetry (DSC)**

DSC is regarded as another valuable analytical technique engaged to study the thermal properties of polymeric materials. It supplies critical information, viz., melting enthalpy, melting temperature ( $T_m$ ), glass transition temperature ( $T_g$ ), crystallization enthalpy and specific heat. In this method, the samples undergo heating procedure until they attain their melting temperature, followed by acquiring a controlled cooling phase under subjugation to an inert atmosphere. This facilitates the proper measurement of physicochemical changes in the sample under consideration by stringent monitoring of the temperature variations as well as controlled heat flow [150, 151].

#### **1.4.4.3. Brunauer Emmett Teller (BET)**

BET is considered as a fundamental methodology to conduct the measurement of specific surface area of solid substances in the domain of surface science and physical chemistry. At its basic core level, this technique relies on the principle that gas molecules, specifically nitrogen gas, adsorb onto the surface of the solid material in order to form a monolayer under exposure to a controlled environmental condition. Researchers tend to determine the specific surface area of the sample by carrying out measurement of the amount of gas adsorbed under varying amounts of pressures. In order to model this adsorption isotherm, BET equation is utilized. Since these days it is regarded as a cornerstone in research domain owing to its extensive applicability in numerous domains; viz., it aids in characterizing porous samples such as biochar, zeolites, etc. and helps in designing effective substances [152].

### **1.5. Testing methods**

#### **1.5.1. Physical testing methods**

The characterization of poly(ester amide)s and their respective nanocomposites involve determination of different physical features, viz., hydroxyl values, acid values, specific gravity, viscosity, and molecular weight. All these attributes offer useful insights into the behavior and compositions of the polymer and their corresponding nanocomposites.

Hydroxyl value of the prepared polymer nanocomposite is assessed using the ASTM E222-17 protocol. This value quantifies the amount of KOH required to neutralize the acid formed through acylation of the hydroxyl groups present within 1 g of the sample under investigation. In this experiment, maleic anhydride is commonly used for conducting acylation under reflux conditions, by using triethyl amine as the catalyst. The carboxylic acid groups formed via acylation are titrated against the standard KOH solution, aided by the presence of phenolphthalein as the indicator [153].

On a similar note, acid value also serve as an important parameter during poly(ester amide) synthesis. It helps to reveal the presence of free carboxylic acid groups in the resulting polymeric material. It is generally observed that as the progress of the reaction increases over time, the acid value parameter decreases on ground of increase in the number of interactions of polybasic carboxylic acids with the polyols which result in reduction in the number of free carboxylic acid groups.

Specific gravity is also considered as an important parameter to evaluate the behavior of the polymer and their corresponding nanocomposites. In order to determine this attribute, ASTM D792 method is utilized which involves insertion of the sample into a suitable solvent inside the pycnometer instrument. This is followed by carrying out measurement of the combined weight of the solvent along with the sample under evaluation. The choice of the solvent portrays an important role in order to ensure that the polymeric sample remains undissolved in the solvent [153, 154].

Viscosity is regarded as another crucial feature that strongly influences the processability of poly(ester amide) resins. It is primarily measured using an Ubbelohde viscometer, although usage of other types of viscometers such as Brookfield, Ford-cup, plate-plate or cone-plate can also be utilized. In general, plate-plate viscometers are used to conduct exploration of rheological features such as variation of viscosity parameter with stress, shear, time as well as temperature. Researchers have tried to study the rheological behavior of poly(ester amide) nanocomposites in order to have a better understanding of the interactions existing between the nanomaterial and the polymer composites. Similarly rheological properties of other polymers have also been scrutinized to predict whether they follow Newtonian or non-Newtonian nature under exposure to shear stress.

Molecular weight is also serving as another crucial parameter that vehemently affects the properties of polymer and their corresponding nanocomposites. Gel permeation chromatography (GPC) is usually utilized to ascertain the molecular weight of polymers, thereby invoking the principle of size exclusion chromatography (SEC) in order to carry out the separation of analytes based on their size. In turn, GPC also facilitates the determination of weight average molecular weight, number average molecular weight, and the polydispersity index parameter.

### **1.5.2. Mechanical testing methods**

The mechanical attributes inclusive of tensile strength, elongation at break, impact resistance and scratch hardness portray an important role in carrying out characterization of polymeric films/sheets intended for their usage as robust materials. These traits play an instrumental role in carrying out assessments regarding suitability of the polymeric materials for their intended utilities. Elongation at break and tensile strength parameters are primarily ascertained using a Universal Testing Machine (UTM) as per the guidelines

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under standard ASTM D882-12 protocol. The films under investigation are cut into rectangular shapes and are subjected to tension prior to their failure to withstand the load of 0.5 kN which permits for the measurement of elongation at break and tensile strength attributes. Additionally, the impact resistance attribute is measured via the standard ball falling method, as outlined specifically in ASTM D1709-16a. Under this protocol, a ball made up of metal is allowed to drop from a specified distance onto some metal plates coated with polymers or the polymeric films under speculation. The resulting impact on the metal plates provides measurement of the polymeric films' ability to withstand the current mechanical forces. Another variable, i.e., scratch hardness is measured using a scratch hardness tester as per the guidelines stated in the ASTM D7027-13 protocol. This test reveals the ability of polymeric films to acquire resistance towards scratching, thereby providing useful insights into its durable nature. These mechanical testing assessments are essential for ascertaining the suitability of these polymeric materials as efficacious surface coating materials, ensuring they meet the requisite performance requirement for their intended utilities [155, 156].

### **1.5.3. Chemical resistance test**

This testing is carried out on polymeric films and their corresponding nanocomposites in order to assess their suitability as surface coating materials in diverse domains. This assessment obeys the ASTM D543-14 standard protocol which involves submergence of the polymeric films in different chemical media, viz., acidic solutions, alkaline solutions, normal tap water, alcoholic solutions, saline solutions, etc. for a specific time period [157]. Subsequently, after the estimated time period, the percentage of weight loss is measured and meticulously analyzed. This testing serves as an important determinant in assessing how well these samples can tolerate exposure to various chemical environments, ensuring that they cope up with the necessary standards required for their intended utilities as robust surface coating materials.

### **1.5.4. UV-resistance test**

This testing is primarily carried out on polymers and their nanocomposites. This testing strictly adheres to the ASTM D5208-14 protocol which involves exposing the polymeric films to UV radiation possessing varying wavelengths for a specified time period under ambient temperature conditions. Subsequently, after exposure, re-evaluation of the



polymeric films was conducted to perceive the impact of the exposure on the mechanical properties, viz., elongation at break and tensile strength as well as on the weight loss profiles. This retesting facilitates determination of the retention percentage which is considered as a tool to measure the polymeric films resistance towards UV radiation [158].

### **1.5.5. Biological testing methods**

#### **1.5.5.1. Biodegradation test**

This test is conducted on polymers and their corresponding nanocomposites under exposure to accelerated circumstances. This testing stringently adheres to the standard ASTM D6691-09 protocol. Under this technique, the polymeric specimens slated for degradation purposes are subjected to an incubated environment bearing a bacterial medium solution comprising of Luria Bertini broth which hosts a specific bacterial strain [140]. Generally, this incubation regime spans around 4-8 weeks, followed by assessment of the biodegradation rates which involve ascertaining the weight loss percentage of the samples along with monitoring the optical density of the bacterial medium solution at regular intervals of time. Subsequently, the degree of biodegradation achieved is highlighted by the turbidity observed in the bacterial medium. This is further correlated with the observed optical density values measured at 600 nm wavelength by using a UV-visible spectrophotometer [159]. The biodegradation of polymeric materials can also be tested by a soil burial test using specific soil conditions.

#### **1.5.5.2. Hemolytic test**

This test is regarded as a preliminary technique to assess the cytocompatibility of polymeric samples. This test puts impetus on ascertaining the rate of lysis or breakdown of the red blood cells (RBCs) when they come into contact with the samples under consideration. In case the RBCs undergo lysis upon exposure to the specimens under investigation, it suggests that the tested specimens are not hemocompatible in nature and vice versa. In order to conduct this test, porcine whole blood is taken, and the RBCs are made to separate from the plasma. Subsequently, the separated RBCs are subject to incubation for a specified duration of time with the samples under investigation. The extent of hemolytic activity is then eventually quantified by carrying out measurements of the absorbance values of the supernatant at 540 nm wavelength [160].

### **1.5.5.3. Cytotoxicity study**

This test stands out as one of the most basic employed techniques for evaluating the toxicity of different materials under consideration. In this regard, human cells are allowed to culture in a specific medium under prescribed controlled conditions, i.e., temperature condition of around 37 °C and CO<sub>2</sub> equipped environmental conditions. Subsequently, the cells are allowed to nurture and eventually, they are exposed to the sample for a predetermined time span. Following this procedure, the cells are made to undergo treatment with 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide(MTT). It is found that MTT is converted into a dark purple colored compound, viz., formazan in the presence of metabolically active cells. The obtained formazan product is then eventually solubilized by invoking the usage of a denaturing buffer solution. Subsequently, the cell visibility is ascertained by conducting measurements of the absorbance values at 570 nm. Therefore, this methodology is successful in providing useful insights into the consequences of the tested specimen on cell viability attribute [160].

## **1.6. Property**

Poly(ester amide)s are known to demonstrate a wide variety of features that consider them useful for different applications. However, the integration of nanomaterials into the poly(ester amide) resin renders not only some novel properties but also aids in enhancing the intrinsic properties of the poly(ester amide) itself. As a result, poly(ester amide) nanocomposites is known to attract a wholesome number of features, some of which are elaborately outlined in the following sections.

### **1.6.1. Physical**

Poly(ester amide) resin and their corresponding nanocomposites are known to possess a plethora of physical properties which are inclusive of color, hydroxyl value, acid value, viscosity, specific gravity, molecular weight, etc. The color of the polymers and their respective nanocomposites and nanohybrids are highly influenced by the colors of the precursors used in carrying out synthesis of the poly(ester amide) resin. Additionally, it is also influenced by the color of the nanomaterials as well as their respective loading amounts into the polymer matrix. Other attributes, viz., hydroxyl values and acid values are indicative of the quantity of hydroxyl groups and free carboxylic acid units present in the synthesized polymer resins. The molecular weight of the polymer is also assessed as

an important variable that significantly influences the solubility and viscosity parameters for carrying out poly(ester amide) production. On the other hand, it is found that higher molecular weights primarily correspond to higher viscosity and lower solubility. This signifies the point that the inherent architectures of the poly(ester amide) resin portray a significant role in assessing the viscosity and solubility parameters. Over the years, it has been found that hyperbranched poly(ester amide)s demonstrate higher molecular weights [161]. However, they possess low viscosity values and are readily soluble in organic solvents. Moreover, an increase in the branching units alters these properties and facilitates upgradation of their properties. This increment in the hyperbranched structure can be attributed to the globular shape of the polymers as well as existence of a wide number of functional groups on the periphery of the polymeric material. Generally, traditional poly(ester amide) resins which are solvent borne tend to be soluble in a wide variety of solvents but remain highly insoluble in water. Nonetheless, it becomes feasible to achieve dispersions of these polymeric systems via usage of neutralizing agents or emulsifiers in the ultimate stage of poly(ester amide) synthesis [162].

### **1.6.2. Mechanical**

Mechanical traits, viz., elongation at break, tensile strength, scratch hardness, impact resistance, and toughness are regarded as pivotal variables when carrying out evaluation for suitability of the polymeric material for manifold practical utilities. Unfortunately, poly(ester amide) nanocomposites are inherently known to demonstrate poor mechanical features, thereby restricting their utility in numerous realms. In order to address this shortcoming and improvise the overall mechanical performance, numerous strategies were unfolded in order to introduce nano-reinforcing agents, robust moieties, as well as non-entangled hyperbranched topology into the poly(ester amide) matrix. Under this context, nanomaterials were incorporated into the main polymer matrix and the results obtained were quite significant. It was found that the polymer nanocomposites exhibited remarkable potency for improvising the mechanical properties exponentially, viz., tensile strength. However, it was perceived that the degree of enhancement hinges on acquiring a homogeneous dispersion of nanomaterials within the poly(ester amide) matrix. Agglomeration or poor dispersion of nanomaterials can often lead to substantial failures. Existing literature lies in agreement with the notion that the integration of various nanomaterials, viz., biochar, CNTs, nanoclay, etc. contribute significantly to the increment

of poly(ester amide) mechanical features. Sari et al. successfully prepared a poly(ester amide) nanocomposite by carrying out incorporation of 1 wt% nanoclay (both in modified and unmodified) forms [163]. The resulting nanocomposites showcased exemplary performance as efficient anti-corrosive materials coupled with improved flexural strength, tensile strength, impact strength and elongation at break. Furthermore, Divakaran et al. demonstrated that the addition of minute amounts of graphene as well as reduced graphene oxide to the polymer matrix resulted in enhancement of elongation at break and tensile strength variables. Rout et al. successfully carried out the preparation of coir-based polymer nanocomposites which are found to be unsaturated in nature along with extensive surface modifications. Furthermore, Salim et al. introduced ZnO nanoparticles into the main hyperbranched polymer matrix, resulting in increment of the mechanical attributes [164]. Recently, Abil et al. studied the influence of addition of talc particles on the polymer coatings and assessed that the incorporation resulted in increment of the mechanical parameters as compared to their crude counterparts [165].

### **1.6.3. Chemical**

The chemical resistance of polymers is a crucial factor that determines their stability as well as ability to maintain their original properties when exposed to various chemical environments, including acidic, saline, and basic conditions. This property is particularly significant for their applications in different surface coatings. The stability of poly(ester amide)s is influenced by their reactivity, which, in turn, depends on numerous factors such as composition, molecular weight, compactness, and cross-linked densities. Poly(ester amide)s containing labile ester linkages tend to exhibit poor chemical resistance, especially when exposed to basic conditions. Additionally, the use of bio-based resources in poly(ester amide) synthesis can make them more susceptible to chemical degradation. To address these challenges and enhance chemical resistance properties, strategies such as creating highly cross-linked hyperbranched architectures and incorporating nano-reinforcing agents into the poly(ester amide) matrix have been employed. The addition of different nanomaterials like clay, silicates, CNTs, etc. have been shown to enhance the chemical resistance of poly(ester amide) and their corresponding nanocomposites. For instance, Ahmad et al. carried out fabrication of reduced graphene oxide incorporated poly(ester amide) nanocomposite and found out that the obtained satisfactory chemical resistance behavior in comparison to the virgin polymer material. Furthermore, Ruban et

al. developed unsaturated polymer nanocomposites containing organically modified montmorillonite as a nano-reinforcing agent and observed improved chemical resistance as the clay content increased in different chemical environments [166].

#### **1.6.4. Thermal**

The thermal properties of poly(ester amide)s encompass their thermal transition behaviors and degradation patterns, providing insights into their thermal stability and suitability for various applications. The thermal stability of polymers is primarily influenced by numerous factors such as poly(ester amide) chain compositions, crosslinking density, the presence of nano-reinforcing agents, and the uniform dispersion of these reinforcing agents within the polymer matrix. Poly(ester amide)s containing aromatic rings and unsaturated bonds in their backbone exhibit higher thermal stability compared to their aliphatic counterparts, as these aromatic rings and unsaturated bonds have elevated degradation temperatures. Generally, poly(ester amide) nanocomposites demonstrate superior thermal properties in comparison to their pristine counterparts. This enhancement can be attributed to the homogeneous distribution of nanomaterials within the matrix, which acts as a thermal insulator, creating a physical and chemical barrier within the polymer matrix. This barrier inhibits the release of volatiles and gases generated during decomposition, thus delaying the degradation process. Additionally, hyperbranched polymer nanocomposites exhibit excellent thermal properties due to their three-dimensional cross-linked architecture, which restricts molecular movement within the matrix. For instance, Alam et al. carried out fabrication of a poly(ester amide) nanocomposite from corn oil with different loadings of silica. It was found that the polymeric materials exhibited improved thermal stability as compared to their pristine counterparts. Subsequently, Rader et al. carried out fabrication of a poly(ester amide) material integrated with cellulose nanocrystals. The prepared nanocomposite material exhibited enhanced thermal properties in comparison to the virgin counterparts. Further literature reveals that incorporation of nanoclay into polymer nanocomposites aid in causing increment of the thermal traits [167-168].

#### **1.6.5. Electrical**

Electrical properties serve as indicators of a polymer's insulating or conducting nature, with conducting polymers finding applications in various fields such as electromagnetic

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interference (EMI) shielding, electrostatic discharge, anticorrosion coatings, capacitors, and more. To confer electrical conductivity to a polymeric material, several key factors come into play. Firstly, the polymer chains must exhibit long conjugation, facilitating the transfer of electrons. Additionally, the incorporation of conducting nanomaterials within the polymer matrix plays a crucial role. The development of polymer nanocomposites involving the integration of nanomaterials like biochar, graphene, rGO, CNTs, etc. has led to improved electrical conductivity. Shahadat et al., for instance, fabricated nanocomposites by combining polyaniline with the main polymer matrix, resulting in materials with notable electrical conductivity. Interestingly, the conductivity increased with higher loading of polyaniline in the polymer nanocomposites. Moreover, Mirsamiei and Faghih explored the usage of multi-walled carbon nanotubes (MWCNTs) into the poly(ether amide) matrix and found that with the increase in the loading of the MWCNTs, there is significant rise in the value of electrical conductivity. In addition, Binti and Raja demonstrated the enhancement of electrical conductivity through the addition of carbon nanotubes (CNT)s to polymer material and its corresponding polymer composites [167, 169].

#### **1.6.6. Optical**

Poly(ester amide) materials exhibit various optical properties, including gloss, transparency, color, fluorescence, and luminescence. Typically, poly(ester amide)s are characterized by their glossy and transparent nature. The addition of small quantities of nanomaterials to the poly(ester amide) matrix tends to have minimal impact on these properties, as the nanomaterials are uniformly dispersed within the matrix, resulting in low light scattering. However, the optical characteristics of poly(ester amide)s can be altered when incorporating specific nanomaterials like reduced graphene oxide, graphene oxide, carbon dots, etc. at higher loading percentages. This may lead to reduced transparency and glossiness. Similarly, the color of poly(ester amide) nanocomposites may undergo change with the addition of larger quantities of nanomaterials. For instance, Mallakpour et al. carried out the synthesis of a poly(ester amide) nanohybrid and incorporated the polymer matrix with zinc oxide and amino-acid functionalized graphene material. Interestingly, the fabricated material exhibited excellent luminescent attributes and showed extensive optical activity. In another study, Zhao et al. created hyperbranched polymer nanocomposites by incorporating ZnS nanoparticles, resulting in materials with varying

refractive indices ranging from 1.48 to 1.65, depending on the nanoparticle loading. Furthermore, luminescent different polymer nanocomposites have been developed, such as those incorporating CD, as demonstrated by Mosconi et al. Additionally, Du et al. achieved luminescence in various polyester materials without the incorporation of nanomaterials, conferring the luminescent properties to different functional groups present in the polyester matrix, which participate in photoluminescence and emit a blue color under UV light [170, 171].

### **1.6.7. Barrier**

Barrier properties in the context of materials, including poly(ester amide)s, refer to their ability to prevent the penetration or transmission of specific substances, such as gases, liquids, moisture, or chemicals. Poly(ester amide)s can exhibit various barrier properties depending on their composition, structure, and processing. It's important to note that the barrier properties of poly(ester amide)s can be tailored and optimized by adjusting their composition, molecular structure, and processing conditions. In turn, it has been closely observed that the enhancement of gas barrier properties in polymers is often achieved via incorporation of various nanomaterials. This improvement can be attributed to the nano-reinforcing agents creating intricate diffusion routes that facilitate gas molecules to navigate, resulting in a reduction in their diffusion rate. For instance, Krook et al. conducted the preparation of a poly(ester amide) nanocomposite integrated with montmorillonite particles. Following this, the barrier property was assessed, and it was noted that this composite exhibited superior barrier traits in comparison to the crude polymers on ground of increased number of diffusion pathway [172].

### **1.6.8. Rheological**

Studying the rheological properties of polymeric materials is crucial for gaining a fundamental understanding of their processability. Rheology involves the investigation of how matter deforms and flows when subjected to applied stress, and this can be done through either steady shear or dynamic oscillatory shear measurements. Steady shear sweeps are commonly used to assess the flow characteristics of polymers by determining their viscosity as the shear rate increases. Additionally, viscoelastic properties such as the loss and storage moduli exhibit phase transition behavior when nanocomposites are formed, transitioning from liquid-like to solid-like. For instance, Wen et al. carried out the

rheological study of poly(ester amide) nanocomposites obtained by integration of silica and polylactide into the polymer matrix. It was found that the nanocomposites showed a tremendous increment in the storage modulus with subsequent increase in the amount of silica/polylactide loading. Moreover, in the case of nanocellulose-reinforced polymer nanocomposites, shear viscosity displayed two distinct regions: shear thinning and Newtonian flow. This behavior was in contrast to pristine poly(ester amide), which exhibited only Newtonian behavior [173]. The introduction of nanomaterials led to strong shear thinning behavior, which resulted in decrease in the viscosity values at low shear rates. Even a minimal 0.5 wt% loading of nanocellulose led to increased shear viscosity in the nanocomposite due to robust particle-particle interactions.

### **1.6.9. Biodegradation**

Biodegradation typically occurs under accelerated conditions, wherein polymer films are exposed to specific bacterial strains and enzymes that facilitate their breakdown and mineralization. In these conditions, the bacterial strains release extracellular enzymes that hydrolyze the chemical bonds within the polymer films, causing surface erosion. Since poly(ester amide) contains labile ester linkages, they are easily hydrolyzed by microorganisms, leading to the depolymerization of the polymer films into smaller, lower molecular weight fragments. These fragments are subsequently broken down by microorganisms and converted into substances such as humus and CO<sub>2</sub> through various metabolic pathways. The biodegradation process of poly(ester amide) typically involves several steps, including water absorption, cleavage of labile linkages resulting in the generation of smaller fragments, solubilization of these fragments, and their subsequent consumption by microorganisms. The rate of biodegradation is influenced by the degree of hydrolysis, referring to the fact that polymers with more hydrolysable linkages tend to biodegrade more effectively. However, the formation of nanocomposites can sometimes impact biodegradability attribute. For instance, Krook et al. carried out the study of montmorillonite infused poly(ester amide) nanocomposites which displayed enhanced biodegradation rate and can be attributed to the presence of more labile linkages in the nanocomposites due to the incorporation of nanoclay. Similarly, Pramanik et al. reported poly(ester amide) nanocomposites integrated with MWCNTs that exemplified loading-dependent improved rate of biodegradation against bacterial strains [174, 175].



### **1.6.10. Biocompatibility**

Different polymers and their respective nanocomposites exhibit excellent biocompatibility, a crucial trait that renders them highly suitable for various biomedical applications. Such materials must undergo *in vivo* toxicity testing and meet the criteria of non-cytotoxicity to be deemed suitable for use. Biocompatibility, in this context, can be understood through two key parameters: biosafety and bio-functionality. Firstly, biosafety entails that the material should not only be non-toxic to the biological system it interacts with but also safe for the surrounding tissues. Extensive research has yielded different polymer materials with exceptional biocompatibility and lack of toxicity, thereby making them ideal for applications such as controlled drug delivery, tissue engineering, biosensing, and more. Secondly, bio-functionality pertains to the material's ability to fulfill specific tasks for which it is designed. Many polymers, in addition to their biocompatibility, possess controlled release capabilities, making them well-suited for sustained drug delivery applications. For instance; Paredes et al. conducted the preparation of a biodegradable poly(ester amide) from L-alanine which was also found out to be biocompatible in nature [176].

### **1.6.11. Catalysis**

The field of photocatalysis has experienced growing demand in recent years, leading to extensive research efforts aimed at enhancing the catalytic properties of photocatalysts. Nanomaterials such as TiO<sub>2</sub>, ZnO, CDs, etc. exhibit excellent photocatalytic properties. When exposed to light, these nanomaterials undergo electron excitation, generating electron-hole pairs. These excited electrons then interact with O<sub>2</sub> and H<sub>2</sub>O, producing free radicals that participate in various catalytic reactions. However, photocatalytic nanomaterials often encounter issues like agglomeration and limited reusability, which can hinder their efficiency. To address these challenges, the concept of creating polymer nanocomposites using photocatalytic nanomaterials has emerged. Photocatalytic polymer nanocomposites serve as heterogeneous photocatalysts with high efficiency, effectively mitigating problems related to agglomeration and reusability. For instance, Abdolmaleki conducted synthesis of a poly(ester amide) incorporated with ZnO and silane moieties coupled with tyrosine linkages which demonstrated excellent photocatalytic activities [177, 178].

## **1.7. Applications**

Poly(ester amide) and their nanocomposites exhibit a wide range of properties, such as mechanical, thermal, biodegradability, optical, barrier, catalytic and electrical characteristics. These versatile properties render them suitable for a diverse array of applications across various fields. Below, an overview of some of these applications utilized in different realms is provided.

### **1.7.1. Paints and coatings**

Poly(ester amide) is widely employed in the formulation of surface coatings and paints. In its resinous state, poly(ester amide) is blended with various additives and then subject to curing or drying processes to create protective films on surfaces. These coatings serve dual purposes: they enhance aesthetics as well as shield surfaces from external factors. Poly(ester amide) coatings offer several advantages, including exceptional chemical and physical properties, transparency, ease of application, and strong adhesion, making them ideal for surface coating applications. The incorporation of poly(ester amide) nanocomposites further enhances the inherent properties of these coatings, while introducing additional features such as antibacterial properties, UV resistance, and corrosion resistance. These enhancements are crucial for various advanced applications. Moreover, the development of nanocomposite coatings allows for increased functionality, enabling the production of waterborne coatings. This transition to waterborne coatings is driven by environmental considerations, as it reduces the usage of solvents and mitigates the release of VOCs, making the coatings more environmentally friendly. For instance; Bakshi and Ahmad introduced a ceria-doped poly(ester amide) nanohybrid that can be successfully utilized as an eco-friendly anticorrosive coating material. Selim et al. developed an alkyd nanocomposite resin by functionalizing sunflower oil and incorporating spherical ZnO nanospheres, resulting in a low-VOC coating with improved physical, mechanical, and anticorrosive properties. Golgoon et al. created various clay/polymer nanocomposite coatings with enhanced anticorrosive properties and other improved characteristics. In addition to their role in coatings, poly(ester amide)s are also employed as adhesives and sealants. Fogelström et al. developed a hyperbranched poly(ester amide) nanocomposite using Boltron H30 polyester and unmodified nanoclay (montmorillonite) as the nanomaterial. This nanocomposite exhibited excellent adhesion, chemical resistance, hardness, flexibility, and scratch resistance [179-181].

### **1.7.2. Electrical**

Poly(ester amide) coatings can serve in electronic devices when conductive nano-reinforcing agents are introduced into the matrix. By incorporating conductive nanomaterials like graphite, rGO, polyaniline, biochar, CNTs, etc. in the poly(ester amide)s, the resulting nanocomposite coatings can become conductive in nature. This conductivity makes them suitable for use in energy storage devices, EMI shielding applications, and anticorrosive coatings. For instance; Pramanik et al. carried out fabrication of castor oil-derived poly(ester amide) nanocomposites incorporated with polyaniline nanofibers. On ground of increased interactions between the nanofiber and the polymer matrix, there was a dip in the sheet resistance values which allowed for its usage as an antistatic material. Similarly, Abazine et al. synthesized poly(ester amide) nanocomposites incorporating MWCNTs that exhibited thermally activated conductivity, making them suitable coatings for electronic devices. Another study by Stone et al. revealed the incorporation of electrospun reduced graphene oxide into the poly(ester amide) matrix which subsequently led to enhancement in electrical conductivity values in the tissue engineering scaffold material [182].

### **1.7.3. Biomedical**

Poly(ester amide)s and their nanocomposites have gained significant traction in biomedical applications, serving various roles such as drug delivery, tissue engineering scaffolds, antimicrobial coatings, and stents, amongst others. The appeal of poly(ester amide)s as biomaterials can be attributed to their favorable features, including strength, flexibility, ease of fabrication into medical devices, biocompatibility, and biodegradability. Desnoyer et al. carried out synthesis of poly(ester amide) based on amino acids, lysine and leucine and the polymer was found to be compatible with the walls of the artery. Under the same backdrop, Pacetti et al. conducted fabrication of poly(ester amide) resin and used this material as coatings for lining up stents for treating thrombosis, restenosis, etc. In addition, Karimi et al. conducted synthesis of a poly(ester amide) material for vascular tissue engineering purpose from amino acids, diols and acids via a melt polycondensation route of preparation [183, 184].

### **1.7.4. Catalytic**

The field of catalysis is actively pursuing synthesis of catalysts which are characterized by

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high efficiency and easy reusability. As a response, the development of poly(ester amide) nanocomposites through the incorporation of nanomaterials like TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO, etc. and others has emerged, given their inherent catalytic properties. These poly(ester amide) nanocomposite films, serving as catalysts, effectively address the reusability challenge owing to their heterogeneous nature. Moreover, their successful integration of nanomaterials into the poly(ester amide) matrix, without encountering issues such as agglomeration, significantly enhances catalytic efficiency. Under this gamut, Moushoul et al. conducted synthesis of various polymeric membranes integrated with various loadings of TiO<sub>2</sub> which facilitated photocatalysis [186].

#### **1.7.5. Wastewater treatment**

Wastewater generated by various industries, such as paints, textiles, battery manufacturing, pharmaceuticals, and more, often contains a mixture of dyes and harmful metal ions. Even at very low concentrations, these contaminants can have significant adverse effects on both the environment and human health. These days, polymer nanocomposites are playing a pivotal role in addressing these environmental issues. Although they come up with their own challenges, various carbonaceous materials such as biochar, CNFs, CNTs, etc. play an important role as adsorbents in removing the toxic heavy metal ions and organic dye molecules on ground of their large surface area. Under this context, Das et al. conducted synthesis of a biochar composite loaded with clay particles to carry out adsorption of methylene blue from wastewater. However, this field remains highly underexplored in the case of polymer nanocomposites which definitely gives a call for extensive research in this genre. [187]

#### **1.7.6. Miscellaneous**

Poly(ester amide)s have found a wide range of applications in various fields, including supercapacitors, fuel cells, liquid crystal displays, textiles, automotive interiors, wire insulation, and more. However, the use of poly(ester amide) nanocomposites, specifically designed with various carbon-based nanomaterials and nanohybrids, is gaining attention due to their potential for cost-effectiveness, making them promising advanced materials for commercial applications.

In recent times, poly(ester amide) nanocomposites have also demonstrated their utility as smart materials, on ground of their ability to exhibit smart properties like self-cleaning and

shape memory when suitable nanomaterials and crosslinkers are incorporated. Moreover, blending poly(ester amide)s with other polymers is becoming increasingly important, as it results in the creation of polymeric materials with unique advanced properties.

Poly(ester amide) nanocomposites offer multifaceted applications, including photoluminescence, anti-reflection, anti-fogging, anti-icing, anti-counterfeiting, anti-graffiti, and more, by incorporating suitable nanomaterials and nanohybrids.. However, these properties have not been thoroughly explored in the context of poly(ester amide) nanocomposites, making it a burgeoning research field within the realm of polyesters [188, 189].

### **1.8. Scopes and objectives**

The aforementioned information provided a conclusive suggestion that bio-derived poly(ester amide)s play a vital role in developing materials that are environmentally friendly as well as sustainable. These bio-based poly(ester amide)s hold the potential to replace harmful commercial alternatives, whether used in their pure form or combined with other nano-reinforcements. By doing so, they contribute to the creation of eco-conscious nanocomposites with remarkable structural properties. These advanced materials have significant relevance across various domains, such as adhesives, structural designs, corrosion-resistant coatings, and drug delivery systems in biomedicine. Moreover, there is a notable gap in the existing literature concerning bio-based poly(ester amide) nanocomposites incorporating carbonaceous nanomaterials like biochar and its modified forms. These nanomaterials can be derived from sustainable, bio-based sources through eco-friendly processes, offering a range of unique and advantageous properties that can be integrated into their respective polymer nanocomposites. Furthermore, the incorporation of these nanomaterials has the potential to enhance all the inherent properties of polymers once the nanocomposites are formed. Thus, the synthesis and exploration of bio-based poly(ester amide) nanocomposites utilizing biochar represents an intriguing and uncharted research avenue in this field.

Taking the above discourse into consideration, the current investigation is guided by the following objectives:

- To conduct the synthesis of a bio-based environmentally benign poly(ester amide) using different types of reactants, viz., citric acid, glycerol, and hexamethylenediamine as the primary precursors.
- To characterize the synthesized bio-based poly(ester amide) using different analytical and spectroscopic techniques.
- To evaluate the thermal, mechanical, and chemical properties of the bio-based poly(ester amide) material.
- To synthesize multifunctional reinforcing agents such as biochar, modified-biochar, etc. along with their structural scrutinization using various analytical and instrumental techniques.
- To incorporate these reinforcing agents into the poly(ester amide) material to obtain the desired poly(ester amide) nanocomposites.
- To characterize the poly(ester amide) nanocomposites and to investigate their thermomechanical performances.
- To apply the prepared poly(ester amide) nanocomposites as advanced functional materials in the field of structural composites, coating formulations, environmental remediation, etc.

### **1.9. Plan of the present work**

To meet the outlined investigation objectives, the subsequent plan of action has been formulated:

- A comprehensive literature survey on the state of art technologies in the sector of bio-based poly(ester amide)s, and their nanocomposites has been fundamentally carried out.
- Bio-based sustainable poly(ester amide) has been prepared using bio-derived raw materials via an environmentally benign route.
- Various stoichiometric ratios of the reactants have been used in the synthesis of the biogenic poly(ester amide)s and the most suitable ratio have been selected for carrying out further extensive study.
- The synthesized resin has been characterized and elucidated by using various analytical and spectroscopic techniques such as FTIR, NMR, UV, TGA, DSC, etc.
- The physical, chemical, mechanical, thermal, and biodegradation properties of the poly(ester amide) material have been assessed using various standard techniques.

- Various sustainable reinforcing agents have been meticulously planned to design and fabricate using potent bio-resources.
- The bio-based poly(ester amide) resin has been integrated with these reinforcing agents to avail nanocomposites for promising traits.
- Explicit characterization of the poly(ester amide) nanocomposites have been carried out using various instrumentation techniques such as TEM, SEM, XRD, XPS, etc.
- The thermal and mechanical features along with the biodegradability attribute of the polymeric nanocomposites have been further enumerated.
- The best-studied poly(ester amide) nanocomposites obtained from optimization via loading of the respective nanomaterial have been significantly utilized for possible potent applications in manifold fields.

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