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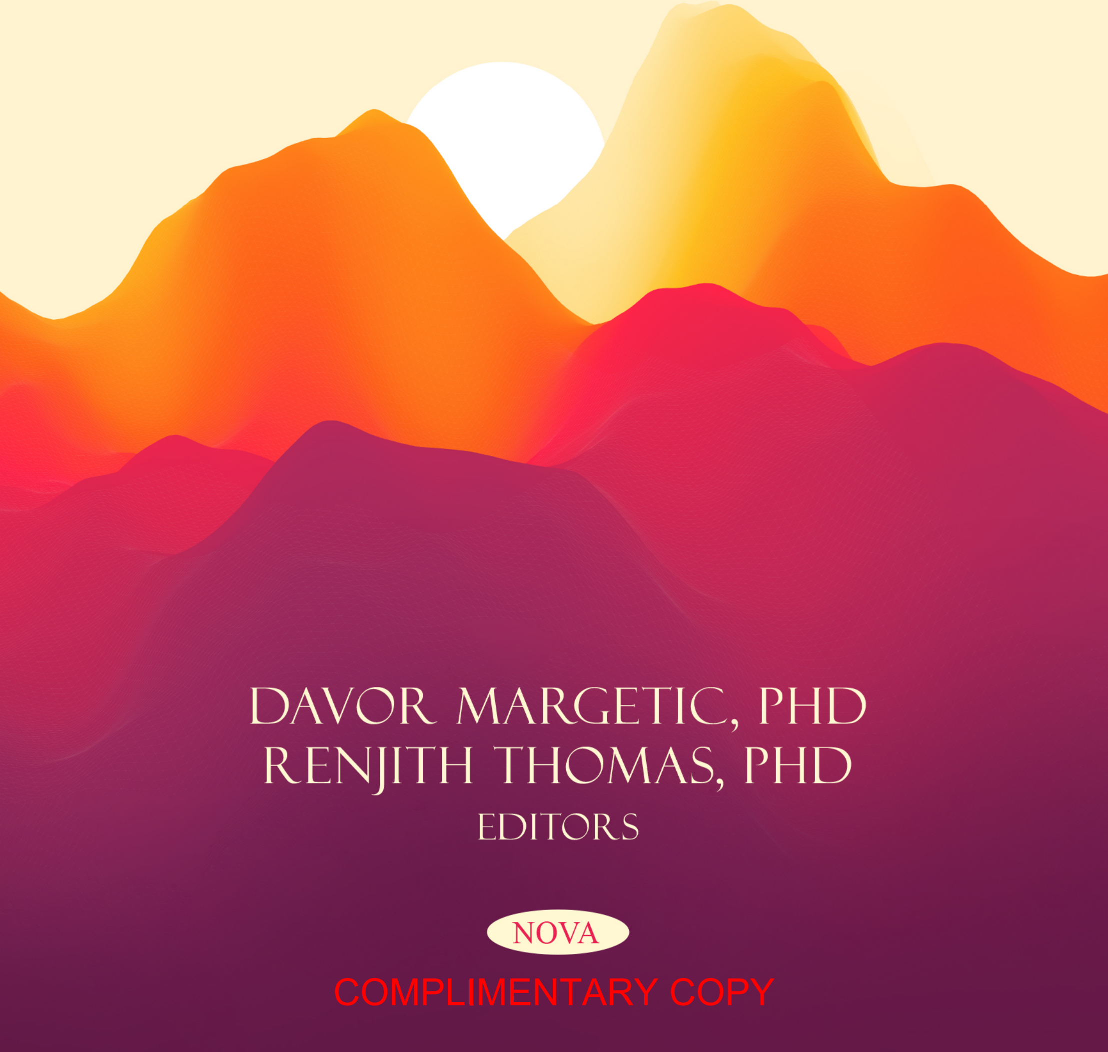

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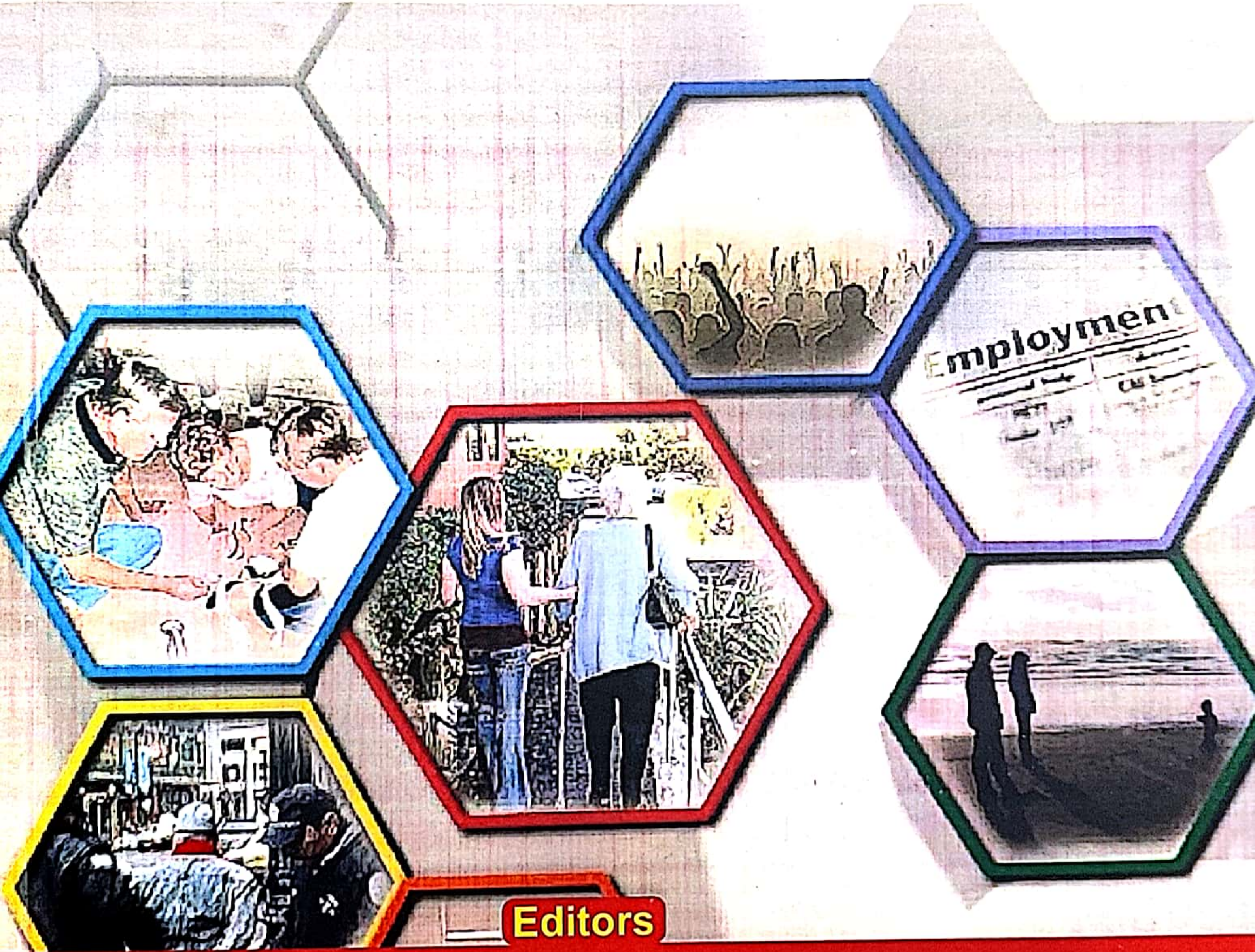

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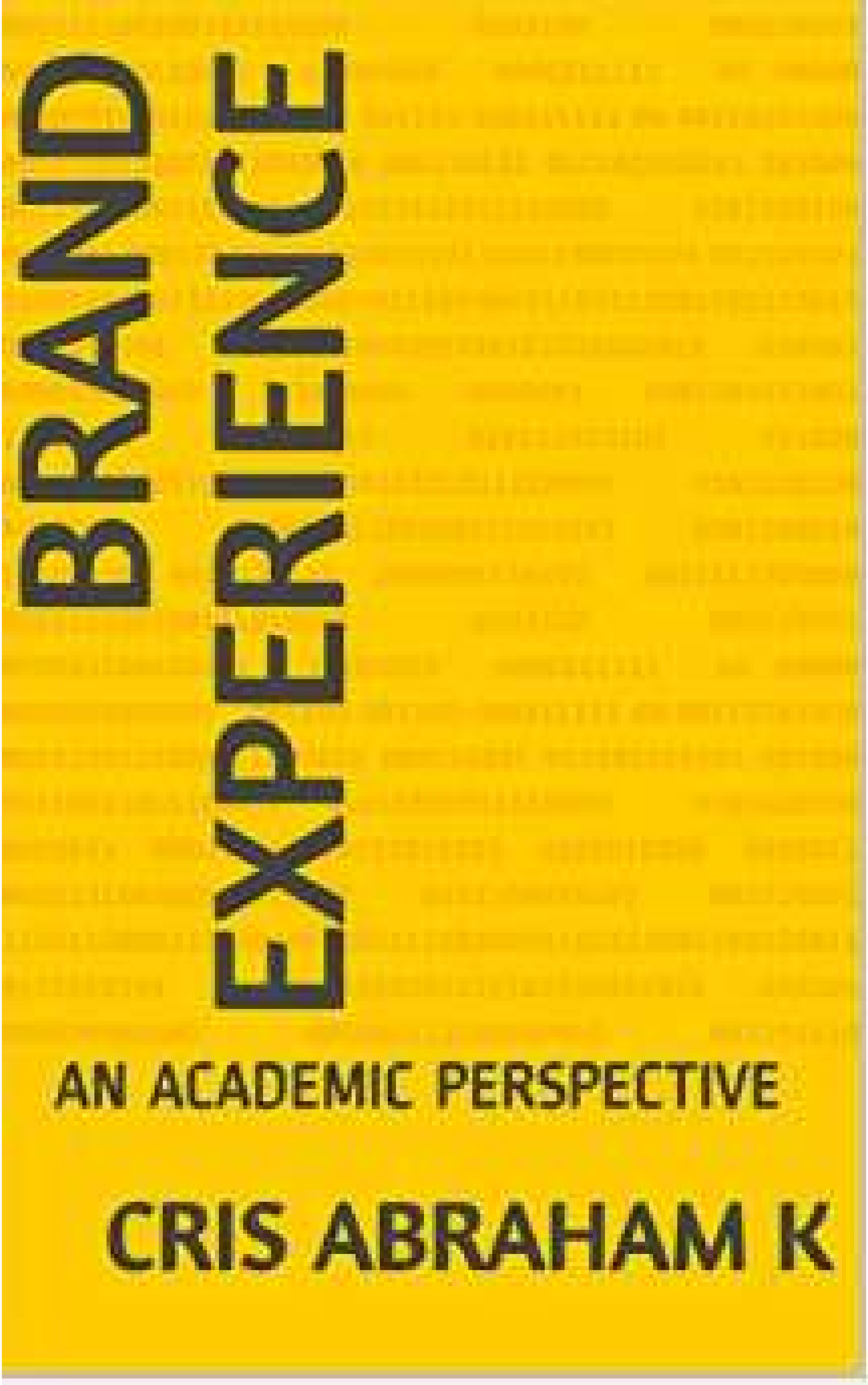

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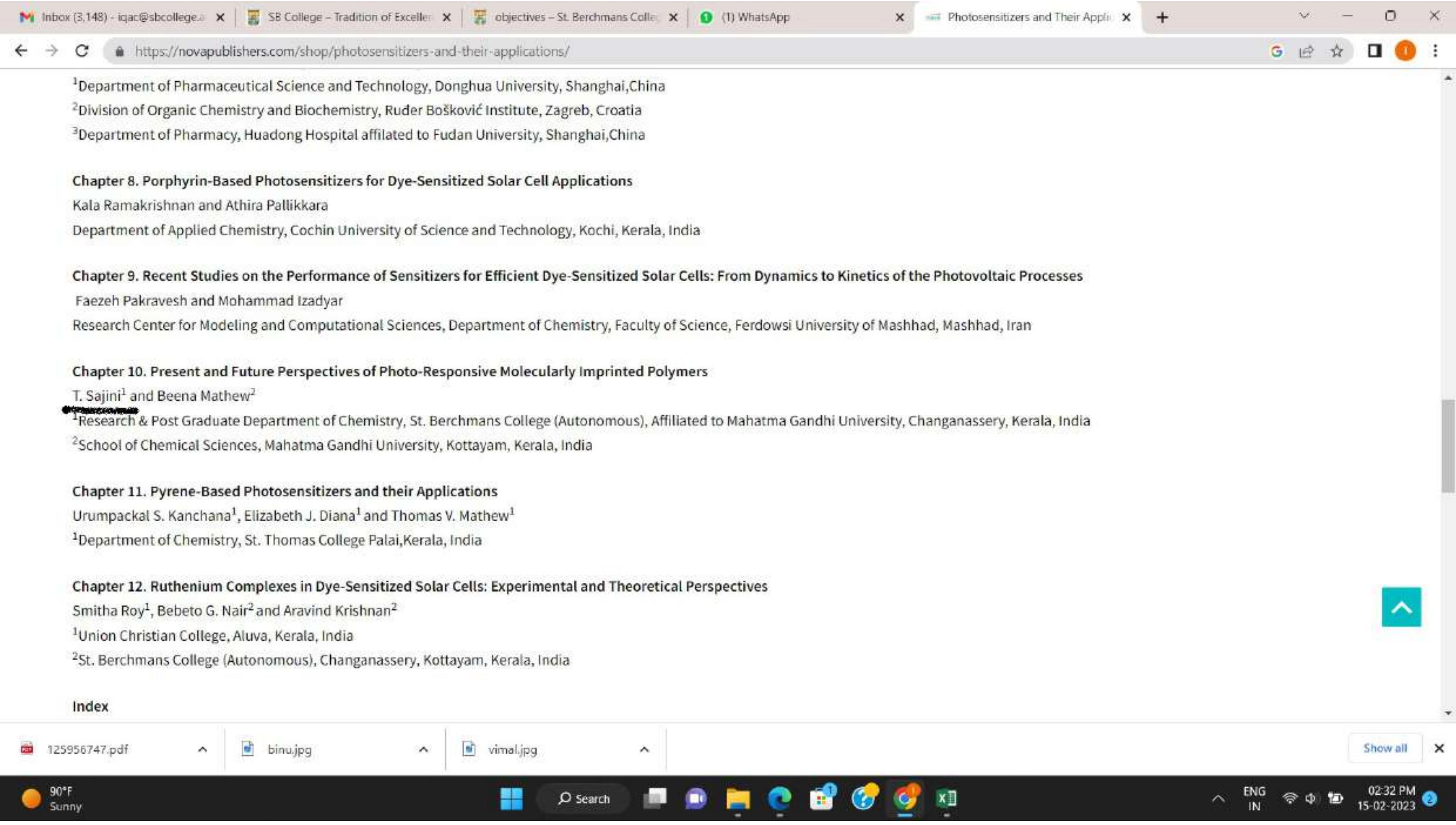

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ELECTROSPUN NANOFIBERS FROM BIORESOURCES FOR HIGH-PERFORMANCE APPLICATIONS

Edited by
Praveen K.M., Rony Thomas Murickan,
Jobin Joy, Hanna J. Maria,
Jozef T. Haponiuk, and Sabu Thomas

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Electrospun Nanofibers from Bioresources for High-Performance Applications

Nanofibers are possible solutions for a wide spectrum of research and commercial applications, and utilizing inexpensive bio-renewable and agro waste materials to produce nanofibers can lower manufacturing costs via electrospinning. This book explains the synthesis of green, biodegradable, and environmentally friendly nanofibers from bioresources, their mechanical and morphological characteristics, along with their applications across varied areas. Additionally, an elaborate idea on the applications of conductive polymers for tissue engineering is given.

Features:

- provides insight about electrospun nanofibers from green, biodegradable and environmentally friendly bio resources
- reviews surface characterization of electrospun fibers
- covers diversified applications such as cancer treatment, COVID-19 solutions, food packaging applications, textile materials and flexible electronic devices
- describes the combined use of 3D printing and electrospinning for tissue engineering scaffolds
- and includes melt electrospinning technique and its advantages over solution electrospinning

This book is intended for researchers and graduate students in material science and engineering, environmental engineering, chemical engineering, electrical engineering, mechanical engineering, and biomedical engineering.

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Preface

Electrospinning is a fiber production method based on the application of electrical forces on a droplet of a polymer solution. Ultrathin polymer nanofibers with diameters down to a few nanometers can be prepared using this technique. A broad range of polymers including polyamides, polylactides, cellulose derivatives, water-soluble polymers such as polyethylene oxide, polymer blends or polymers containing solid nano-particles or functional small molecules can be electrospun. Using various electrospinning techniques, a wide variety of micro and nano materials can be produced, this includes nanofibers, nanobelts, Janus nanofibers, Janus nanobelts, hollow nanofibers, coaxial nanofibers, and coaxial ribbons. The main advantages of electrospinning are the simplicity and low cost of the processing system, the short time required to prepare continuous 1D structures and its versatility, enabling the production of fibers and membranes with a wide range of morphologies and materials.

The depletion of petroleum resources and the toxicity of the solvent, has motivated research to look into alternative electrospinnable materials to produce cheaper and more environmentally friendly carbon fibers. One of the main challenges associated with the production of bio fibers through the electrospinning process are its low viscoelastic properties. It is expected that blending bioresources such as lignin with small amounts of synthetic polymers can improve its spinnability. However, to reach the published results among the scientific fraternity a structured book with a detailed table of contents is required.The chapters of this book are structured in this manner. Following paragraphs depicts a detailed overview of different chapters in this book

The main objective of Chapter 1 is to give the reader a general review on the history of electrospinning, important governing factors in electrospinning, its material properties, extraction of nanofibers from biobase polymers such as polysaccharides, proteins, lignin, and so forth, and its applications such as food packaging, tissue engineering, sensor applications, and the like.

Chapter 2 reviews developments in the field of biofibers, biopolymers and biocomposites witnessed in recent years due to its major advantages such as renewability, biodegradability, low cost, light weight and high specific strength. A comprehensive summary of the recent development of biomaterials, biofibers, biopolymers, biocomposites and the electrospinning process is presented in this chapter. A review of the performance of biomaterials, their major applications and the future prospects of biofibers are also included.

Chapter 3 highlights some insight into how to manufacture high performance nanofibers by understanding their morphology, mechanical strength, and so forth, in relation to the electrospinning process. It also discusses the relationship between the various characterization processes such as SEM, TEM, AFM, and the like, with the electrospinning process.

Chapter 4 discusses the spectroscopic techniques for the characterisation of electrospun polymer nanofibers. These techniques help to carry out structural and molecular analyses of polymer fibers prepared through electrospinning. FTIR and Raman spectra help to identify the backbones of polymer fibers by identifying the functional groups present in the fibers. XRD spectra identify the crystalline and amorphous backbone and peak position. UV-Visible spectroscopy helps to identify the absorption bands of the samples. Photoluminescence spectra help to identify the emission region of the electrospun polymer fibers. Thus, a polymer fiber is fully identified and unveiled by using different spectroscopic techniques, thus helping to use them for various applications.

Chapter 5 gives an overview of polysaccharides, or poly carbohydrates consisting of long chains of monosaccharide units connected by glycosidic linkages with huge amount of carbohydrates. In this chapter the various types of polysaccharides, their different properties, and their potential for use in food packaging applications is discussed. Characteristics such as biocompatibility, a non-toxic nature, abundance, and low cost makes them suitable candidates for future food packaging industries.

Chapter 6 discusses needleless electrospun nanofibers for drug delivery systems. The author proposes that this work will serve as a useful guide for a drug delivery industry to process a nanofiber on a large and continuous scale with a blend of drugs in the nanofiber, using wire electrode electrospinning and also as a useful guide to obtain a high-quality nanofiber from a needleless electrospinning process for drug delivery application.

Chapter 7 illustrates application electrospinning to create conductive scaffold materials. To create a conductive scaffold material, the process of electrospinning proves to be a highly impactful process. Tissue engineering and drug delivery are the two important aspects, discussed in this chapter. Potential conductive polymers are explained in detail along with the applications of conductive electrospun membranes.

Chapter 8 gives an overview of the electrospinning process for the fabrication of nanofibres in protective textiles. Protective textiles or technical textiles are basically used where high performance or functional characteristics are of prime importance.The prime focus of this chapter is to explain the possibilities of electrospun nanofibers in various protective textiles. Applications of electrospun nanofiber web for protective textiles such as for antimicrobial protection, chemical protection, thermal protection, and the like, are discussed in detail.

Chapter 9 discusses combining melt electrowriting (mew) and other electrospinning-based technologies with 3D printing to manufacture multiphasic conductive scaffold for tissue engineering. This chapter discusses successful tissue scaffolds which can be fabricated by various methods such as electrospinning, freeze-drying, 3D printing and self-assembly techniques, where the scaffolds must have appropriate chemical composition, desired cytocompatibility, mechanical stability, biodegradability, sufficient hydrophilicity, porosity, suitable morphology, and roughness to be considered as ideal substrates for controlling cellular interaction and cell fate.

Due to the biocompatibility of bio nanofibers, these have been widely used as water purification membranes. Bio nanofibers from the electrospinning technique, recent trends, future scope of bio nanofibrous membranes in water purification applications, an so forth, are the topics discussed in Chapter 10.

In comparison to the various fabrication processes for energy storing devices, electrospinning proves to be more economic, industry viable and more flexible. Various aspects like the need, advantages and development of biomass derived electrospun nanofiber based materials for energy storage applications were discussed in detail in Chapter 11.

Usage of electrospun polymer nanofibers in flexible electronics such as biosensors, transistors, energy storage devices, and the like, proves to be of great advantage. Chapter 12 provides a summary about the latest advancement in the design and development of flexible electronic devices employing electrospun polymer nanofibers followed by highlighting the future perspectives for electrospun polymer nanofiber-based flexible electronic devices.

Chapter 13 briefly discusses different types of electrospun bio nanofibers and their applications in protection against Covid 19. How the improvements were made related to the filtering efficiency and breathability in personal protective equipment (PPE) like face masks, protective clothing, and the like, via various studies, are discussed in this chapter. In the future perspectives section, the incorporation of nanoparticles, drugs and herb extracts into the electrospun nanofibers, along with the employment of more biopolymers, which helps to improve their antipathogenic activities and biocompatibility, are also discussed.

As far as the area of air purification and protective clothings is concerned, electrospun bio nanofibers play a major role. The use of bio nanofibers ensures reusability and recyclability while developing the green materials. Chapter 14 discusses the need for an air purification system. It also gives an introduction to basic electrospinning techniques, relating to bio nanofibers and green electrospinning. Applications in the air filtration domain such as the fabrication of facial masks and protective clothing are also covered along with the future aspects of bio nanofibers.

For the last two decades, enormous efforts have been made towards the development of electrospinning technology but still there are some challenges which need to be resolved. Chapter 15 gives an insight into the strategies being followed to scale up the electrospinning system from lab to industry. Explanations given in this chapter show that electrospinning is a promising and facile technique to produce nanofibers and has huge potential for scaling up in industrial applications.

There is no doubt that the electrospun nanofibers will emerge in more diverse shapes and sizes and will find application in a variety of domains such as sound adsorption, battery applications and from cosmetics to catalysis.

Editors

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Dr. Praveen K.M. is an Assistant Professor of Mechanical Engineering at the Department of Mechanical Engineering, Muthoot Institute of Technology and Science, Kochi. Praveen obtained his Bachelor of Technology in Mechanical Engineering from the University of Calicut and Master of technology (MTech) in Integrated Design and Manufacturing from Amrita Vishwa Vidyapeetham. Praveen pursued his PhD in Materials Engineering from at the University of South Brittany (Université de Bretagne Sud),Lorient, France. Prior to his PhD Dr. Praveen worked in the faculty in Mechanical Engineering at SAINGITS College of Engineering, Kottayam. He specialised in the area of polymers and their composites. During his research career he has edited eight books and published research papers in reputed journals such as Elsevier, Springer, Taylor and Francis, and others. Praveen was also instrumental in delivering talks in national and international symposiums and conferences. Currently he is guiding four PhD students in collaboration mode. He also has worked and associated with the Jozef Stefan Institute, Ljubljana, Slovenia; The Mahatma Gandhi University, India; and the Technical University in Liberec, Czech Republic, Gdańsk University of Technology, Poland. His current research interests include polymer matrix composites, fiber reinforced composites, plasma surface engineering of polymers and fibers, polymeric materials for shielding applications, surface modification of cellulosic surfaces, nano composites, and nanocellulose based composites.

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1 Some Insights on Electrospun Nanofibers from Bioresources

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1.1 INTRODUCTION

The fascinating and unique properties of a one dimensional nanostructure such as a nanofiber, used in the nonwoven form has gained immense attention in energy storage and generation, sensors, agriculture, medical, pharmaceutical and textile industries, water purification, environmental remediation and so on [1]. Various techniques, including melt blowing, gelation, vapor phase polymerization, centrifugal spinning, directed electrochemical nanowire assembly, and template synthesis method are used for the fabrication of nanofibers [2]. Among these different techniques, electrospinning is considered as a versatile, simple, and direct method for the fabrication of thin/ultrathin fibers from polymer solution or from melts, with the diameter of the fibers reaching down to the nanoscale [3].

The concept of electrospinning dates back to the 1600s when William Gilbert observed that in the presence of an electric field, a cone shaped water droplet was formed which eventually became known as the Taylor cone in later years [4]. In the 1900s, John Francis Cooley, originally from Penn Yan, New York, filed the first patent on electrospinning. In his patent, he proposed four types of indirectly charged spinning heads including a conventional head, a coaxial head, an air assisted model, and a spinneret featuring a rotating distributor. In addition, he also proposed the recovery of the solvent and the use of a dielectric liquid as the medium instead of gas. In his three electrospinning patents, he used a Wimshurst-type influence generator, pyroxylin (nitrocellulose) as the test material and introduced benzole as the co-axial head on the outside of the fiber, which is presumed to prevent the clogging of the nozzle due to the premature evaporation of the ether [5]. Between 1907 and 1920, John Zeleny, a physicist at the University of Minnesota, published a sequence of papers on the discharge of electrical charges from solid and liquid surfaces. He studied the shape effect of a cylindrical electrode and atmosphere (pressure, temperature, and humidity) on the discharge current and concluded that the principal factor was the diameter of the electrode, rather than the shape. He worked on the behavior of fluid droplets at the metal capillary ends which inspired the effort to mathematically model the behaviour of fluids under electrostatic forces [6,7].

Although the concept of electrospinning has been known since the 1600s, the technique has gained popularity from the 1930s solely because of Anton Formhals, who contributed significantly in the form of patents. Between 1931 and 1944, Formhals published 22 patents on electrospinning [8]. He invented the saw-tooth emitter for the distribution of spinnable fluid and developed a multi-head spinneret to fill up spinnable fluids individually to produce short fibers also known as staple fibers [9]. In his first patent in 1934, Formhals described the apparatus to produce artificial threads using electrical charge [10] and in 1940, he filed another patent describing a method to produce (i) composite fibers from multiple polymers and (ii) fiber substrate by electrospinning polymer

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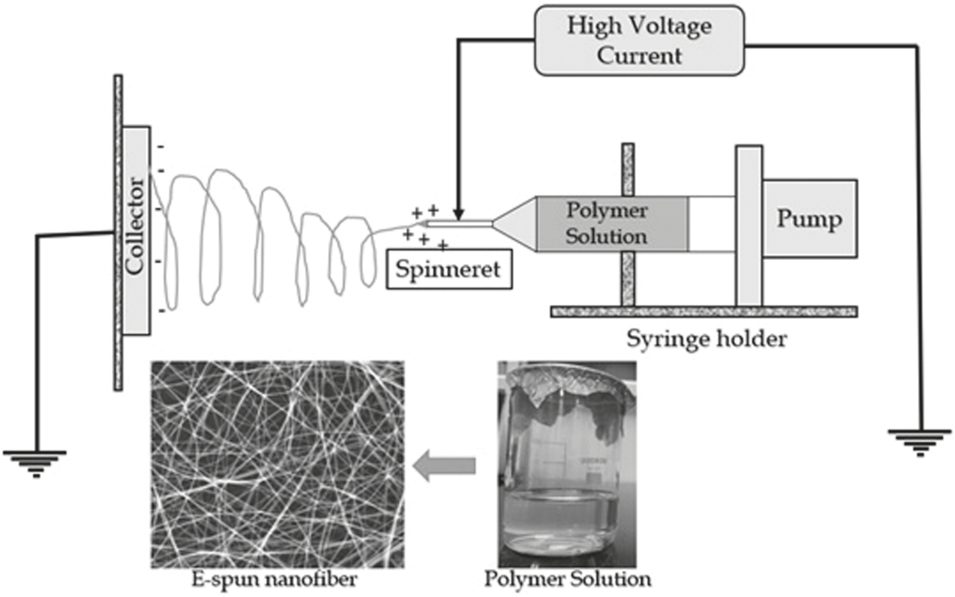

FIGURE 1.1 Schematic representation of the electrospinning process

fibers on a moving base substrate [11]. In 1938, Igor' Vasil'evich Petryanov-Sokolov and Natalya D Rozenblum fabricated electrospun fibers from nitrocellulose feedstock, which they developed into filter materials known as 'Petryanov filters' [8]. Between 1964 and 1969, Sir Geoffrey Ingram Taylor studied the jet forming mechanism and the shape of the droplet from the tip of the capillary tube. His results demonstrated the formation of cone shaped droplets when an electric field was applied to the tip of the capillary tube. This is now referred to as the 'Taylor Cone'. He also accurately stated that at an angle of 49.3°, the surface tension of the polymer can be balanced [12]. From 1990s, several publications were made available to the scientific community and patents have been filed on electrospinning. Many scientific publications demonstrated the application potential of electrospun nanofibers for a myriad of applications.

1.2 ELECTROSPINNING AND ITS GOVERNING FACTORS

Electrospinning or 'electrostatic spinning' is a voltage-driven process governed by electrohydrodynamic phenomena where fibers are developed from a polymer solution/polymer melt. The main components of the electrospinning unit comprise of (i) a high voltage (HV) power supply or the applied voltage (AV), (ii) a needle assembly or spinneret that includes pump, syringe, and needle, and (iii) a ground collector for the deposition of fibers. Three steps are involved in the formation of fibers which includes the initiation of the jet, bending instability and solidification/deposition of the fiber. The electrospinning process is initiated by the application of a high electric field to the polymer solution in the needle. Upon continuous application of high voltage to the polymer solution, the droplets acquire charge and elongate the polymer to form a cone, commonly known as the 'Taylor cone'. The jet ejected from the Taylor cone thins down along its travel path towards the collector and this mode of jetting is termed as electrohydrodynamic cone-jetting [13]. The charged ions from the electrospinning jet creates a repulsive force causing the jet to undergo bending instability [14]. As the jet travels, it elongates due to simultaneous events occurring separately, namely, the solvent getting evaporated from the polymer, that deposits as a fiber, and the repelling of charges within the polymer from each other [15]. This results in the formation of thin to ultrathin nanofibers that are deposited on the collector. This is termed as stable electrospinning. Likewise, unstable electrospinning happens when the polymer jet breaks into droplets as the electrostatic force of the polymer is not overcome by the critical voltage. This is known as ‘Plateau-Rayleigh instability’ which leads to the formation of broken fibers [16,17].

1.2.1 Parameters Influencing the Electrospinning Process

The spinning of nanofibers from the polymer solution is largely governed by certain critical parameters. The process/operational parameters include applied voltage, feed rate, tip to collector distance and the solution parameters such as polymer concentration, molecular weight, viscosity, surface tension and conductivity. Altering these two parameters can develop diverse fibers from various polymers with requisite fiber diameter and structural morphology. Significant works have been carried out to characterize the properties of fibers connected to the process and solution parameters. Each parameter is explained briefly for an overview on its effect on fiber formation.

1.2.1.1 Process/Operational Parameters

1.2.1.1.1 Applied Voltage

Applying a high-voltage power to the polymer solution in the spinneret plays a crucial role because it provides surface charge to the electrospinning jet and influences the diameter of the nanofiber [18]. Application of a high electric field to the polymer droplet charges the surface of the liquid. As a result, the electrostatic force surpasses the surface tension of the liquid, resulting in the ejection of an electrically charged jet from the tip [19]. The electrostatic force controls the formation of a Taylor cone in the spinneret, thereby influencing the diameter of the nanofiber. Several studies reported the formation of ultrathin nanofibers, due to an elevated electrostatic repulsive force on the charged jet by increased applied voltage [20–23]. Further increasing the voltage beyond the critical value will decrease the size of the Taylor cone and increase the velocity of the jet at a constant flow rate. This will result in the formation of a beaded nanofiber [19,24]. A study also reported that the diameter of fibers did not show any significant variation at different applied voltages ranging from 10 to 20 kV [25].

1.2.1.1.2 Flow Rate

The fiber morphology is also determined by the rate of flow of polymer solution from the spinneret. The critical flow rate varies according to the polymer solution, and it aids in the development of bead-less and smooth electrospun nanofibers. With an increased flow rate beyond the critical limit, drying of the nanofiber jet during its projection between the needle tip and metallic collector is reduced [26]. In addition, the elevated flow rate also results in the development of a nanofiber with beads, ribbon-like defects and unspun droplets [27]. A research study systematically investigated the correlation between flow rate and the electric field and stated that the flow rate is directly proportional to the electric field [28].

1.2.1.1.3 Tip to Collector Distance

The distance between the tip of the needle and the collector, also known as tip to collector distance (TCD), is another influential parameter in determining the fiber morphology which alters rendering of the polymer solution in a similar way to the applied voltage and flow rate. The time to deposit nanofibers on the collector, evaporation rate of the solvent, and whipping or the instability interval also depends on the tip to collector distance. Therefore, an optimum distance must be maintained to develop smooth, uniform and bead-free electrospun nanofibers. Numerous research projects have been conducted to determine the effect of the TCD on the size of nanofibers. The results concluded that a large diameter nanofiber was developed when the distance was smaller, and the diameter was reduced by further increasing the distance between the needle and collector [29–32].

1.2.1.2 Spin Dope/Solution Parameters

The solution parameters are the intrinsic properties of the polymer solution including the polymer concentration, molecular weight of the polymer chain, solution viscosity, electrical conductivity, and surface tension of the liquid dispersion which determines the structural morphology of the fiber.

1.2.1.2.1 Polymer Concentration and Solution Viscosity

The concentration of the polymer decides the borderline for the formation of fibers during electrospinning as it is directly related to the solution viscosity and surface tension. At lower polymer concentration, the viscosity of the solution is reduced, and it contributes to the formation of drops instead of the fiber, due to the fragmentation of the polymer chain into droplets before it reaches the collector [33]. Increasing the viscosity by increasing the polymer concentration improves the chain entanglement within the polymer chain. In the nanofiber jet, viscoelastic force competes with the surface tension, thus resulting in the development of bead-free smooth electrospun nanofibers [34]. This concentration is the critical concentration for the particular polymer to develop into a nanofiber and it varies according to the choices of polymer. Increased polymer concentration beyond the critical point disrupts the movement of polymer solution from the capillary due to cohesion [29].

1.2.1.2.2 Molecular Weight

The molecular weight of the polymer affects the entanglement of the polymer chains in solutions. At constant polymer concentration, the low molecular weight polymer tends to develop beads [35] while the high and ultrahigh molecular weight tends to develop a micro-ribbon morphology [36,37]. In some cases, the electrospinning process does not depend on molecular weight if the intermolecular interactions are sufficient for fiber formation [19]. In a study, smooth phospholipid nanofibers were spun from the polymer solutions containing lecithin at a concentration higher than 35 wt% [38].

1.2.1.2.3 Viscosity

The viscosity of the polymer solution largely depends on the concentration of the polymer and its molecular weight. Formation of different morphological fibers including smooth fibers, beaded fibers, and ribbon-like fibers is facilitated by the viscosity of the solution. In solutions having low viscosity, it was observed that the surface tension dominates, which leads to the formation of beaded nanofibers. Conversely, a high viscosity solution inhibits the flow of the solution through the needle tip and at optimum viscosity, smooth and continuous bead-free fibers are produced.

1.2.1.2.4 Surface Tension

The initial and most important step in the electrospinning process, ‘jet initiation’ is significantly governed by surface tension. The polymer solution droplet at the tip of the needle is formed when the electrostatic forces overcome the surface tension of the emerging liquid jet [18]. The most influencing factors of the surface tension in a solution are the solution’s components including the choice of solvent [39]. A study also reported that changing the mass ratio of solvent mix can alter the surface tension as well as the solution’s viscosity [19].

1.2.1.2.5 Conductivity

The formation of a Taylor cone, achievement of a nanofiber of the required size and morphology are determined by the conductivity of the solution. The solution conductivity or the charge density is mainly controlled by the type of polymer, the solvent, and the addition of salts. Compared to a synthetic polymer, the polyelectrolytic nature of the bio-polymer subjects the polymer jet to higher tension in the electric field, resulting in the poor fiber formation [40]. An ideal dielectric polymer solution carries less charge in the solution to move onto the surface of the liquid, therefore, the electrostatic force generated by the application of the electric field will be insufficient for the formation of the Taylor Cone. However, a conductive polymer contains free charges which move onto the surface of the liquid, and this facilitates Taylor Cone formation and initiates the electrospinning process [34]. The electrical conductivity of the solution can be altered by using organic acids as solvents or by the addition of ionic salts which aids in the development of a fiber with a smaller diameter [41]. Research studies on the effect of solution conductivity on the formation of nanofibers indicates that raising the solution conductivity supports the formation of thinner fibers [42].

1.3 NANOFIBERS DERIVED FROM BIOSOURCES/BIO-POLYMERS

Several hundreds of polymers including natural, synthetic and composites are fabricated into nanofibers using the electrospinning process**.** The main advantage of bio-polymers is their ability to mimic the chemical environment of nature primarily by biocompatibility and biodegradability, which is not seen in synthetic counterparts. However, the complex structure of these natural polymers and weak mechanical properties results in fragile materials in comparison to synthetic polymers [43]. The following sections provide insights into the bio-polymers, or the polymers derived from the bioresources used in electrospinning.

1.3.1 POLYSACCHARIDES

Polysaccharides are long repeating units of monosaccharides (sugars) that are linked by glycosidic bonds. The varying diversity of polysaccharides is based on their chemical structure, chemical composition, molecular weight, and ionic character. The feasibility of the electrospinning process for the formation of polysaccharide nanofibers depends on the degree of their chain, the polymer concentration, chemical composition and structure, and shear thinning properties of polysaccharides [44].

1.3.1.1 Cellulose

Cellulose is the key component of plant cell walls and is the first abundant natural bio-polymer available in the universe. Bio-polymers are widely available, biodegradable, cost-effective and renewable [45]. The chemical structure of cellulose constitutes of a linear chain bio-polymer consisting of (1,4)-linked β-D-glucose units having asyndiotactic configuration [46]. The prime natural source of cellulose is the lignocellulosic material that is present in wood (40–50 wt%). The other sources include vegetable fibers such as cotton, jute, flax, ramie, sisal, and hemp. In addition, bacteria, algae, fungi, and some animals (for example, the tunicate) also produce cellulose [47,48].

Spinning of cellulose dates to 1855, when George Audemars patented a process for spinning collodion: cellulose extracted from mulberry (*Morus alba*) trees. He experimented by simply dipping a needle into the collodion solution, and drew it out, producing a long thread of rapidly hardening collodion [8]. In 1934, Formhals, first patented the electrospinning of cellulose derivatives, cellulose acetate and propionyl cellulose using pure acetone and alcohol as solvent mixed with 1 g of solactol and palatinol as softening agents [10]. In 1938, Igor' Vasil'evich Petryanov-Sokolov and Natalya D Rosenblum developed Battlefield Filter (BF) which was spun from cellulose acetate prepared in a solvent mixture containing ethanol and dichloroethane [49].

Cellulose possesses strong inter- and intra- molecular hydrogen bonding and hence it is insoluble in common solvents and can dissolve in dimethylsulfoxide/paraformaldehyde, sulfur dioxide, and so forth. However, due to its physical properties, these solvents evaporate rapidly and are unsuitable for the electrospinning process[50–52]. Solvents such as N-methyl morpholine N-oxide/water (nNMMO/H_2O), lithium chloride/dimethyl acetamide (LiCl/ DMAc), ionic liquids and ethylene diamine/salt have been studied for the formation of cellulose nanofibers. These solvents possess low volatility and cannot be completely removed during the process of electrospinning. Hence, removal of these solvents serves as a limiting factor for the formation of cellulose nanofibers [53]. Therefore, the ether derivatives such as cellulose acetate, cellulose acetate phthalate, cellulose acetate butyrate, cellulose acetate trimelitate, hydroxypropylmethyl cellulose phthalate, and ester based cellulose derivatives like methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, carboxymethyl cellulose, and Sodium carboxymethyl cellulose, and so on, are used for electrospinning, although compromising cellulose's ability for delayed degradation and structural stability [46,52,54].

The most used cellulose derivative is cellulose acetate (CA) which is formed by the mixture of cellulose, acetic acid, and acetic anhydride with subsequent addition and later neutralization of a small quantity of sulfuric acid during processing [46]. Crystallinity of CA and insolubility in water can be reduced by the acetylation of cellulose [55]. The major characteristics of CA that make it popular include biodegradability, biocompatibility, non-toxicity, high affinity, mechanical performance, better hydrolytic stability, relative cheapness, and exceptional chemical resistance [56]. The weak intramolecular hydrogen bonding of CA makes it soluble in simple solvents such as acetone, tetrahydrofuran, *N*,*N*-dimethylformamide (DMF), chloroform, dichloromethane (DCM), methanol (MeOH), formic acid (FA), and pyridine or mixed solvents such as acetone-DMAc, chloroform-MeOH, and DCM-MeOH [46]. The solubility varies according to the degree of substitution of the hydroxyl group by the acetyl group per glucose unit [57]. Numerous beaded-fibers were obtained with CA solution prepared using acetone as the solvent, which is due to the low boiling point of acetone whereas, when CA solution was prepared using a binary solvent, acetone-DMAc, stable nanofibers were obtained with a fiber diameter ranging between 100 nm to 1 μm [58,59]. Research was conducted to study the effects of a single solvent system and of multiple solvent systems on the architecture of electrospun CA fibers together with consideration of the solution and process parameters. The study suggested the use of binary solvents or multiple solvent systems such as acetone-DMAc (1:1, 2:1, 3:1), DCM-MeOH (4:1) which was effective in fabricating smooth fibers [60]. In another work, the effect of a binary solvent containing acetic acid and water on the fiber formation of CA was studied. It was shown that 17 wt% CA solution prepared using 3:1 acetic acid and water on a weight basis, resulted in nanofibers with mean diameter of 180 nm [61]. Other solvent systems, and CA concentrations for the fabrication of nanofibers along with the fiber diameters is given in Table1.

Ethyl-cyanoethyl cellulose [51], ethyl cellulose [62], hydroxy propyl ethyl cellulose [63] are a few other derivatives of cellulose spun in to cellulose based fibers. Ethyl-cyanoethyl cellulose (E-CE)C was prepared from ethyl cellulose and acetonitrile. Porous (E-CE)C nanofibers were fabricated by using tetrahydrofuran (THF) as the solvent and the smallest fiber diameter obtained was 200 nm. The applied voltage influenced the crystallinity and the diameter of the fibers. With increased voltage, the crystallinity and the average fiber diameter increased. However, further increasing the voltage decreased the crystallinity of the fibers [51]. Fabrication of ethyl cellulose nanofibers using single and multi-component solvent systems, was investigated. The composition of the multicomponent solvent system (THF–DMAc) greatly influenced the diameter and the distribution of the electrospun ethyl cellulose nanofibers. Smaller mean diameter and narrower diameter distribution of the fibers was obtained in the multicomponent solvent system than with those prepared with a single component solvent system. The morphological analysis of the fibers revealed tiny tubercles on the surface of the fibers which was formed due to the difference in volatilization of the two components in the multi-solvent system [62]. Hydroxy propyl cellulose (HPC) nanofibers were developed using two different solvents namely: anhydrous ethanol and 2-propanol with various process and solution parameters. The average fiber diameter of HPC and the bead formation were both influenced by the nature of the solvent and the applied voltage [63]. Electrospun nanofiber, hydroxypropyl methylcellulose (HPMC) has been developed from two different HPMC derivatives with similar molecular weights and varying degrees of the substitution groups. The two cellulose derivatives vary mainly in methoxy content. The diameter of both nanofibers was measured to be 128 and 127 nm. In addition to that, similarity in nanostructures was observed, indicating that the methoxy content of the HPMC exerts a negligible level of influence on the nanofiber formation [64].

TABLE 1.1
The effect of cellulose acetate concentration and solvents on fiber diameter

Cellulose Acetate Concentration	Copolymer Concentration	Solvent Used	Average Fiber Diameter	Reference
8 wt%	-	Acetone/DW = 5:1	300–500	[65]
14 wt% (Mw-25000 g/mol)	-	Acetone/DMF = 1: 4	170 ± 40 nm	[66]
20 wt% (Mw-61000 g/mol)	-	Acetone/DMAc=2:1	750 nm	[67]
16 wt% (Mw-30000 g/mol)	-	Acetone/DMAc=2:1	385 nm	[68]
17 wt% (Mw-30000 g/mol)	-	Acetone/DMAc=2:1	701–1057 nm	[69]
15 wt%	-	Acetone/DMAc=2:1	200nm	[70]
5 wt/v % (Mw-30000 g/mol)	-	DCM/Acetone=1:1	300–1000nm	[71]
7.5 wt/v % (Mw-30000 g/mol)	-	DCM/Acetone=2:1	75–1500nm	
10 wt/v % (Mw-30000 g/mol)	-	DCM/Acetone=3:1	1500–3500nm	
14 wt%	-	Acetone/Benzyl alcohol=2:1	3.41±1.78 µm	[72]
14 wt%	-	Methyl Ethyl Ketone/ Benzyl alcohol=4:1	2.03±0.66 µm	
18 wt%	-	Acetone/DMSO=2:1	650±130nm	
15 wt. %		Acetone/DMF=2:1	80–140 nm	[73]
17 wt/v%	-	Acetone and N-N DMAc=2:1	598 nm	[74]
17 wt/v%	-	Acetone/DMF=2:1	587nm	[75]
17 wt%	15 wt% PVA	CA – Acetone/DMF (2:1) PVA – Distilled water	~340–740nm	[76]
20 wt %	3 wt/v% PEO	CA – 99.9% AcOH PEO – 90%EtOH	950–1170 nm	[77]
15 wt%	3 wt% Polyhedral Oligomeric Silsesquixoanes (POSS)	Acetone/DMAc=2:1	262±59nm	[78]
15 wt%	5 wt% POSS	Acetone/DMAc=2:1	262±50nm	
Mw=50,000 g/mol	Silk Fibroin	CA-Acetone/DMF=2:1 SF-Formic acid	154.54 ± 83.51 nm	[79]
20 wt%	CA: Zein=12:8	Acetic acid:water = 70:30, v/v	98±17nm	[80]

1.3.1.2 Chitin

Chitin is the second most abundant extraordinarily versatile natural polymer next to cellulose and is considered as one of the most promising bio-polymers for fabricating advanced materials [81]. These polysaccharides are of marine origin and are found in crustacean exoskeletons (shells) and mollusks, as well as in insects and fungi [82]. Chitin is a neutrally charged bio-polymer and this makes it insoluble in most organic solvents [83]. However, due to strong inter and intra-molecular hydrogen bonds through acetamido groups and high crystallinity, chitins are soluble in solvents like 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), hexafluoroacetone, chloroalcohols in conjunction with aqueous solutions of mineral acids, and DMAc containing 5% LiCl [83,84]. Depolymerization of chitin by gamma irradiation improved the solubility of chitin and using HFIP as the solvent, chitin nanofibers were developed with fiber diameter ranging from 40–640 nm [85]. A research study was focused on the development of nanocomposite fibers with chitin whiskers and a synthetic biodegradable polymer such as poly (vinyl alcohol) (PVA). Nanofibers developed at 5.1% chitin whiskers to

PVA ratio had maximum tensile strength and with further increase in the chitin content, the tensile strength of the mat was reduced [86]. In another study, chitin was blended with poly (glycolic acid) (PGA) in HFIP and electrospun nanofibers of average diameter 140 nm and diameter distribution between 50–350 nm [87] were obtained. The same research group blended chitin with silk fibroin in HFIP to obtain chitin composite nanofibers. The diameter of the fibers reduced from 920 nm to 340 nm when the concentration of chitin in the blend increased [88]. Water soluble chitin based nanofibers were developed by blending carboxy methyl chitin with PVA and the developed fibers were crosslinked with glutaraldehyde vapors followed by thermal treatment [89]. Gamma irradiation of chitosan powder with Cobalt 60 reduced the molecular weight of chitosan from while it increased the solubility. Chitin nanofibers were developed by dissolving irradiated chitin powder in HFIP. The developed chitin nanofibers showed an increase in the degradation rate compared with the commercially obtained chitin microfibers [90]. Addition of chitin nanofibrils to the chitosan solution facilitated the formation of nanofibers and decreased the bead formation during spinning due to increased viscosity, increased shear rate and decreased surface tension [91].

1.3.1.3 Chitosan

Chitosan is a polyaminosaccharide with unbranched molecular units that act as monomers. These functional monomers consist of active primary amine, primary and secondary hydroxyl groups on its molecular chain β-(1–4)-2-amino-2-deoxy-d-glucose [92]. Deacetylation of chitin leads to the formation of chitosan, that is, when the degree of deacetylation (DD) of chitin reaches approximately 50%, it becomes soluble in aqueous acidic solution. During the process of deacetylation, the polysaccharides are converted to polyelectrolytes in the acidic medium. Hence, the properties of chitosan in solution largely depends on the degree of deacetylation, molecular weight, polymer charge, ionic strength, and pH.

Fabrication of smooth, bead-free, pure chitosan nanofibers can be achieved when the spin dope solutions are prepared with low molecular weight chitosan and using strong organic acids as solvents that have low boiling points and dielectric constants and low pH (less than 6.5) [93]. With increased pH, the polymer molecules tend to lose their charge and precipitate out of the solution because of amine groups being deprotonated [46].Using trifluoroacetic acid as a solvent, nanofibers of chitosan with molecular weight 210000 g/mol were fabricated [94]. In another experiment, concentrated acetic acid was used as a solvent along with the application of a very high electric field to electrospun chitosan nanofibers with mean fiber diameter of about 130 nm [95]. A study suggests that alkali treatment hydrolyzes the chitosan molecule thereby reducing the molecular weight, which in turn facilitates the electrospinning process [96]. A comparison study with high and low molecular weight chitosan in fiber formation leads to the conclusion that high MW chitosan did not produce fibers due to the accumulation of the higher charge densities of chitosan molecules containing more amino groups per molecule compared to the low molecular weight chitosan [97]. Attempts were made to generate pure chitosan nanofibers using new generation electrospinning, in other words, Nanospider technology. Due to high viscosity, chitosan nanofiber was difficult to spin even using the latest technology [98]. Therefore, it is evident that the electrospinning of pristine chitosan is difficult due to the excessive surface tension of the chitosan solution, polycationic nature in solution, strong hydrogen bonds, high molecular weight, and wide distribution of its molecular weight [85,95,96]. Hence, blending it with synthetic or natural polymers with good ability for fiber formation and better miscibility with chitosan serves as a solution for improving the spinnability. However, electrospinning of chitosan blends will still be difficult if the concentration of chitosan exceeds the concentration of other polymers in the blend [97].

1.3.1.3.1 Chitosan and Synthetic Polymer Blend

The fiber formation ability of chitosan was improved by blending it with a biodegradable polymer such as poly (vinyl alcohol) (PVA) [99], poly (ethylene oxide) (PEO) [100], poly lactic acid (PLA)

[97], polylactic-co-glycolic-acid (PLGA) [101] and so on. In a study using PVA as a copolymer to blend with chitosan, the molecular weight of chitosan was halved by alkali treatment using 50% aqueous sodium hydroxide at 95ºC for 48 h. Reduced molecular weight improved the uniformity of polymer composition and fiber formation efficiency, thus, producing smooth nanofibers with less beads and diameter of fibers ranging from 20 nm to 100 nm [102]. Poly (ethylene oxide) is another polymer suitable for the development of chitosan nanofibers. In 2008, chitosan nanofibers with average diameters in the range of 62 nm to 130 nm were fabricated by blending chitosan with PEO solution in acetic acid. The results from the study showed that the number of beads in the nanofibers decreased with increased total polymer concentration, indicating that the formation of nanofibers depends on the solution concentration. In addition, it was also observed that the fiber diameter decreased as the concentration of chitosan increased [100]. Chitosan composite nanofibers were prepared, along with poly lactic acid (PLA) by the process of co-axial electrospinning in the form of core/shell layers in which PLA and chitosan form the core and shell layers, respectively. The diameter of the chitosan composite nanofibers developed by co-axial electrospinning was measured to be approximately 303 nm with a double layer structure [97]. By the process of emulsion electrospinning, chitosan nanofibers were developed along with polylactic-co-glycolic-acid (PLGA). In this study, PVA was used as an emulsifier which was later extracted from the fibers by immersing them in 50% ethanol for 8 h with subsequent drying in an oven overnight [101]. Research was conducted to obtain pristine chitosan nanofibers after blending chitosan with a copolymer. In this study, with a different ratio, PEO was added to the chitosan solution prepared using 0.5M acetic acid. By increasing the concentration of PEO from 20 to 40% in the polymer blend, bead-free smooth fibers were obtained with average diameters ranging from 85 to 150 nm respectively. Neutralization of the nanofibers obtained was carried out using potassium carbonate in water or 70% aqueous ethanol, as solvent with subsequent repeated washes using pure water to extract carbonate salts, potassium acetate and PEO. The NMR analysis of the nanostructure proved the complete removal of PEO and the salts from nanofibers thus producing pure chitosan nanofibers [103].

1.3.1.3.2 Chitosan and Natural Polymer Blend

Other than synthetic polymers, the spinnability of chitosan was improved by blending it with natural polymers such as hyaluronic acid [104], sericin [105], zein [106], cellulose derivatives [107], gelatin [108] and so on, where the different chemical structures of the polymers being used lead to enhanced properties in the prepared nanofibers [102]. In 2007, chitosan based hybrid nanofiber mat with average diameter of 300 nm was developed using hyaluronic acid by a wet spinning method [104]. Sericin is another natural polymer that exhibits good compatibility with chitosan. The polymer solution blend was prepared by dissolving it in trifluoro acetic acid (TFA) with 3 wt% total polymer concentration and the mass ratio was varied at 1/1, 2.5/1, 4/1, and 5/1. Smooth, continuous, and uniform diameter distribution between 240 nm and 380 nm was observed in the 2.5:1 mass ratio of chitosan and sericin. The developed nanofibers exhibited excellent antibacterial properties against both gram positive and gram negative bacteria [105]. Hollow fibers with high chitosan content were developed using cellulose acetate as a copolymer using a non-acidic organic dope solvent. Chitosan nanoparticles of 50–150 nm was synthesized by the addition of a surfactant, sodium dodecyl sulfate (SDS) into chitosan solution. The polymer blend was prepared by mixing cellulose acetate with the chitosan nanoparticles and then electrospinning. The developed nanofibers were highly porous with good mechanical properties and with high chitosan content [107]. Hydrophobic fiber mats with efficient biocide properties were prepared from the composite of chitosan and a corn prolamin, zein. The bio-polymer solution of zein and chitosan was prepared by dissolving zein in ethanol at room temperature and chitosan in TFA at 37º C. They were mixed in the solvent proportion of ethanol/TFA of 2:1 (wt/wt). A total polymer concentration of 25 wt%, with different blend ratios of zein to chitosan such as: 99/1, 97/3, 95/5 and 90/10 (wt/wt), were subjected to electrospinning with 0.20 ml/h flow-rate, 14 kV applied voltage and 10 cm distance from tip-to-collector. Bio-polymer blends containing below 5 wt% of chitosan in the formulation generated clear continuous ultrathin bead-free fibers. As the ratio of chitosan increased in the bio-polymer blend, the shape of the fibers was smaller with increased beaded regions in the fibers [106]. A nanofiber based biosensor was developed using chitosan-gelatin composite for immobilization of enzyme. In this study, chitosan and gelatin blend was prepared using 60% acetic acid. The polymer blends with volume ratios of chitosan to gelatin solution of 50:50, 40:60, 30:70, and 20:80, respectively were prepared and subjected to electrospinning with constant flow rate of 1.6 mL/h, 20 cm tip to collector distance and applied voltage of 20 kV. At 40:60 chitosan and gelatin ratios, ultrathin nanofibers without any beads were obtained [108].

1.3.1.4 Pullulan

Pullulan is a natural, linear, neutral, non-hygroscopic polymer mainly composed of maltotriose units connected by α-(1,6) glycosidic bonds, and maltotriose consisting of three glucose units connected by α-(1,4) glycosidic bond [109]. It is a food-grade and water-soluble exo-polysaccharide produced by polymorphic fungus *Aureobasidium pullulans* grown in starch and sugar media. Pullulan is a non-toxic, non-mutagenic, non-carcinogenic, biodegradable, and edible polymer with considerable inter-molecular mechanical strength [110]. Uniform fibers of pullulan were developed up to a concentration of 22 wt% using various solvents including double distilled water [111,112], DMSO and water mixture [113], formic acid [114].

Pullulan nanofibers with average fiber diameter between 100 to 700 nm were obtained using water as the solvent. The effect of the solution and process parameters on the morphology and diameter distribution of pullulan nanofibers was studied. The results concluded that 22 wt% polymer concentration, 31 kV applied voltage, 20 cm tip to collector distance and 0.5 ml/h flow rate are the optimum parameters for the development of pullulan nanofibers [112]. Like other polymers mentioned earlier, pullulan was also blended with many synthetic and natural polymers to fabricate pullulan nanofibers. In 2013, pullulan was blended with amaranth protein isolate (API) to develop ultrathin fibers of polymer blend with improved thermal stability. Initially, phase separation was observed when the two polymers were dissolved in two separate solvents (water for pullulan and formic acid for API) and then blended. Later, it was observed that pullulan is soluble in formic acid and hence both polymers were dissolved in 95% formic acid. The ratio of API and pullulan was varied at 50:50, 60:40, 70:30 and 80:20 based on weight. In the ratios of 50:50 and 60:40, continuous bead-free fibers were obtained with a diameter of 300 nm. When the protein content was higher it produced less stable nanofibers and hence certain surfactants were required to produce defect-free fibers [114]. In the same year, another study was conducted to blend pullulan with β-cyclodextrin for the encapsulation of bioactive volatile compounds. A polymer solution containing 20% pullulan and 10% β-cyclodextrin was prepared using water as solvent and 90% of the active ingredient was added. The solution was subjected to electrospinning with various process parameters. At 0.5 mL/h flow rate, 15 kV applied voltage and 12 cm tip-to-collector distance, a bio-polymer nanofiber was obtained. Since, pullulan is a water soluble polymer, the release of an encapsulated compound was attributed to the change in the relative humidity [115]. Pullulan/montmorillonite (MMT) clay nanocomposite was prepared in aqueous solution and fabricated into nanofibers. Uniform fibers with an average diameter of 50–500 nm was developed from the 20 wt% of pullulan containing different amounts of montmorillonite clay (1–10 wt%) [111]. The other method for the fabrication of pure pullulan nanofibers was the electro-wet-spinning method. The electrospinning unit comprises of a high voltage generator, pump and grounded metal mesh immersed in pure ethanol. The non-woven mat gets deposited in the ethanol coagulation bath which will be washed using pure ethanol and dried in a desiccator under vacuum. This is called an electro-wet-spinning method. Pullulan solution was prepared using a binary solvent containing DMSO and water. The diameter of fibers increased as the concentration of DMSO increased. At 12% (w/v) polymer concentration, bead-free continuous nanofibers were obtained. It was also found that the coagulation bath was not required when the concentration of DMSO was less [113]. Pullulan-alginate nanofibers were electrospun from aqueous polymer solutions by the method of free-surface electrospinning. Aqueous pullulan solutions (10 wt%) were developed into beaded nanofibers with a broad diameter distribution of 110 nm in diameter. The addition of 0.8 to 1.6% (w/w) alginate to the 10% (w/w) pullulan solution, produced continuous and smooth fibers with smaller fibers ranging from 87 to 157 nm in diameter which is due to the increase in polymer chain entanglement, and enhanced hydrogen bonding interaction between pullulan and alginate [116].

1.3.1.5 Cyclodextrin

Cyclodextrins are low molecular weight cyclic oligosaccharides consisting of 6, 7, or 8 (α, β or γ - cyclodextrins) glucose units linked by α-(1→4) glycosidic bonds. Structurally, they are truncated cone shapes which contain hydrophobic inner cavities owing to the $-CH$ and $-CH_2$ carbons and ether oxygens and hydrophilic outer surface due to the high number of hydroxyl groups. Being an intriguing amphiphilic molecule, cyclodextrin favors the non-covalent host guest interactions with a variety of molecules, thus, serving as an excellent carrier for the encapsulation of many compounds and also as a packaging material [201].

Electrospinning of low molecular weight molecules is difficult due to the lack of chain entanglements. However, cyclodextrin possesses unique physical-chemical properties such as self-assembling behavior, which makes it possible for electrospinning [118]. The development of cyclodextrin nanofibers without the use of a carrier polymer matrix was first reported in 2010, where methyl-beta-cyclodextrin (MβCD) nanofibers were electrospun. Various concentrations of MβCD solution were prepared from 100% to 160% (w/v) using water and N,N-dimethylformamide (DMF) as two types of solvent. Thinner fibers were obtained from the solution prepared using water than when prepared using DMF, due to low viscosity and high conductivity. Conversely, smooth fibers were developed by using DMF as solvent and this is due to the high boiling point of DMF (153° C). The evaporation of solvent during the electrospinning is slowed down when solvents with high boiling point are used, thus resulting in the development of a smooth fiber. This study revealed the development of pure cyclodextrin nanofibers using two different solvent types and reported that the major governing factors for the electrospinning of the cyclodextrin nanofibers are the type of solvent, solution concentration and intermolecular interactions between the molecules [119]. Similarly, gamma cyclodextrin (γ -CD) nanofibers were obtained from a DMSO–water (50/50 v/v) solvent system without using any carrier polymeric matrix. The spinnability of γ-CD was due to the presence of hydrogen bonding, high solution viscosity and viscoelastic solid-like behavior in a DMSO–water system [120]. Another study reported the fabrication of ultrathin hydroxypropyl-β-cyclodextrin (HPβCD) fibers from highly concentrated aqueous solutions. The fiber formation ability of HPβCD solution is due to the aggregation of HPβCD molecules at high concentrations, as demonstrated by the increase in viscosity and bound water concentration [121]. A similar result was observed when DMF was used as a solvent for the preparation of hydroxypropyl-β-cyclodextrin fibers [122]. DMF was also used as an ionic solvent for the preparation of β-cyclodextrin nanofibers without using any carrier polymer. DMF decreased the viscosity of the solution resulting in better spinnability and development of fibers in the nanometer range [123]. Recently, the research team has studied the development of hydroxypropyl-alpha-cyclodextrin (HP-α-CD) nanofibers from an industrial perspective. In this study, the solution conductivity was varied by preparing the solution in distilled water, tap water and salt water (1% NaCl, w/w). It was observed from the study, that the higher solution conductivity was the dominating factor to obtain bead-free ultrathin nanofibers. However, less uniform HP-α-CD nanofibrous web was developed from a polymer solution prepared from salty water having higher solution conductivity [124]. Although, cyclodextrin nanofibers can be developed without the addition of any carrier polymer or copolymer, certain active compounds require addition of other natural or synthetic polymers for stimuli-response release.

1.3.2 PROTEINS

Proteins are bio-polymers with linear/unbranched chains of amino acids that possesses a complex 3D architecture, with several levels of structural organization/hierarchy including strong inter- and intra-molecular attraction [46]. Their biocompatibility, unique structural and functional properties, and nutritional value have gained interest in developing biomaterials based on protein and peptides. They exhibit various unique conformational, physicochemical, and biological properties which can be exploited for the delivery of bioactive compounds [46]. Proteins have a broad range of applications, yet it is very hard to process into fibers. Aqueous protein spin dope solutions tend to have high surface tensions. Also, polypeptides are polyelectrolytic in nature which has limited chain entanglements in aqueous solutions. Hence, the jetting process is hindered. The formation of several beaded fibers and development of droplets instead of continuous fibers are observed during the spinning process [125]. Despite, a variety of proteins, either alone or in a blend with several organic or biocompatible polymers, like PEO, poly caprolactone (PCL), Poly (lacto-co-glycolic acid) (PLGA), PVA, and the like, have been electrospun and applied in a variety of fields, including drug delivery, filtration, sensors, tissue engineering and so on. The blending of protein with compatible polymers reduces the extent of protein denaturation required to develop fibers to retain their bio functionality and to provide mechanical stability [126]. In this section, we will broadly overview proteins like zein, silk protein, bovine serum albumin (BSA), Soy protein isolates, and whey protein isolates.

1.3.2.1 Zein

Zein is the major storage protein of corn or maize which comprises 50–60% of the total protein found in the endosperm [127]. It is classified as prolamin, as it contains large amounts of amino acids including proline, glutamine, leucine, and alanine and possesses high thermal stability and oxygen barrier properties [128]. Due to the presence of hydrophobic amino acids in higher proportion, zein is insoluble in water but soluble in aqueous alcohol solutions [125]. Due to good biocompatibility, biodegradability, non-toxic nature and film-forming properties, zein is considered to be a promising polymer for the development of biobased materials [129]. Zein can be electrospun into nanofibers using aqueous ethanol, however, due to high surface area it exhibits poor water stability and mechanical strength which is considered as the limiting factor for its application. Zein nanofibers swell and distort into films thereby decreasing the number of interconnected pores and surface area which eventually decreases its tensile strength [130]. Hence, to address this issue, various attempts were made, including crosslinking and blending with other polymer compounds. As crosslinking agents, citric acid [130], oxidized sucrose [131], hexamethylene diisocyanate (HDI) [132], aldehydes [133, 134], and carbodiimide (CDI) [135] are used. The most efficient crosslinking agents such as small molecules like aldehydes are proven to be toxic and carcinogenic while cross-linking procedures with citric acid and disaccharide derivatives, tend to be complex and energy-consuming [136–138]. Therefore, preparing a nanocomposite solution by blending zein with other polymers overcomes this disadvantage of zein nanofibers.

Pure zein nanofibers with diameter of 700 nm were fabricated using 80% aqueous ethanol as a solvent. The result of this study shows that the fiber formation depends on the polymer concentration as well as on the applied voltage. When the concentration of zein was over 21 wt%, the voltage applied for the fiber development was 15 kV, while increasing the voltage supply to 30kV resulted in fibers being formed even at a lower concentration of 18 wt% [139]. In another aspect, the effects of process parameters such as polymer concentration, solvent content, flowrate, applied voltage, needle tip-to-collector distance and pH to control the fiber size and morphology were studied. The results show that under acidic pH conditions, the viscosity of the solution increases due to protein agglomeration and fibers appeared to be in the form of sheets whereas under alkaline condition, protein oligomerization prevented fiber formation. Due to molecular structure and a high solvent removing efficiency, the thermal properties of zein were improved in zein nanofibers compared to zein cast films [140]. The developed zein nanofibers were tested for their efficiency in encapsulating the light sensitive active compound, β -carotene, and the study proved that light stability was increased when exposed to UV radiation for the encapsulated compound [141]. Without crosslinking, the structural stability of zein in aqueous solution was improved by blending it with silk fibroin. Ribbon like fibers were developed when zein solution was prepared using aqueous ethanol as a solvent. Zein/silk fibroin solution prepared using formic acid produced dense fibrous structured nanofibers with approximate fiber diameter of 230–260 nm. Increased silk fibroin content improved the tensile strength of the blend fibrous membranes while it decreased its Young's modulus [142]. Zein nanofibers generated were incorporated as reinforcements for a poly (lactic acid)/poly (ethylene glycol) (PLA/PEG) matrix and it reduced the oxygen permeability of the matrix by 70% without altering the melting and crystallization behavior of the PLA/PEG matrix [143]. Zein/cyclodextrin hybrid nanofibers were developed by preparing the polymer blend solution in DMF. The solution was subjected to electrospinning with applied voltage of 15 kV, flow rate of 0.5 mL/h and the tip-to-collector distance of 12 cm. Improved thermal properties with higher glass transition temperatures and higher degradation temperature was observed in the blend nanofibers compared to pristine nanofibers [129]. Similarly, addition of cellulose acetate also improved the thermal stability and glass transition temperature. A series of Zein/CA hybrid nanofibers were electrospun using DMF and acetone as a solvent respectively and the developed fibers were characterized using advanced instrumentation techniques. Pristine zein nanofibers developed from the solution containing DMF as a solvent resulted in circular morphological fibers due to the high boiling point during electrospinning. From the study, it was shown that zein/CA nanofibers can be developed conveniently and the characterization of the same in TGA and DSC revealed the improvement in thermal stability, increased degradation temperature and thermal stability [144]. Similarly, addition of tannin also improved the glass transition temperature of the nanofibers [145]. Gelatin/zein nanofibers fabricated *via* hybrid electrospinning exhibited good solvent resistance against water or ethanol, with respect to the pristine nanofibers [146]. The encapsulation efficiency of bioactive volatile compounds like hexanal in zein nanofibers was improved by adding poly (ethylene oxide) (PEO) to the solution blend. The addition of co-polymer PEO aided in stimuli responsive release of the encapsulated volatile compound in response to the increased relative humidity [147].

1.3.2.2 Silk Protein

Silk is a natural bio-polymer consisting of two main proteins: silk sericin and silk fibroin. The sticky protein found outside of the silk strands are silk sericin which accounts for 15–35% of silk cocoons. By the process of degumming, sericin is removed to obtain more versatile protein, Silk fibroin [148]. The amino acid sequence of silk fibroin varies depending on species, however, in general hydrophobic units are comprised of glycine, alanine, and serine residues while hydrophilic units consist of charged amino acids which provide the elasticity, high tensile strength, and formation of β-sheets within the protein. The secondary structure of silk also varies according to specific sequences which in turn affects the mechanical properties, thermal stability, chemical characteristics, and solubility [148–150]. The most used silk protein is the silk fibroin extracted from *Bombyx mori* silkworm. It exhibits excellent biocompatibility, bioactivity, biodegradability, tunability, and mechanical stability [148,151].

The first silk nanofiber developed by the process of electrospinning was patented in 2000[152]. The nanofiber was fabricated from natural silks of *Bombyx mori* and *Nephila clavipes* from solutions in hexafluoro-2-propanol with the approximate diameter of the fibers of 200 nm [153]. Nanofibers of silk fibroin from two species (*Bombyx mori* and *Samia cynthia ricini*) and of the recombinant hybrid fiber comprising the crystalline domain of *B. mori* silk and non-crystalline domain of *S.c.ricini* silk from hexafluoroacetone (HFA) solution was fabricated using an electrospinning method [154]. Using Response Surface Methodology (RSM), silk fibroin nanofibers were generated, and the effects of process and solution parameters was analyzed on the diameter of the fiber. It was found that the polymer concentration of the solution governed the average fiber diameter while the applied voltage did not affect the diameter of nanofibers at low polymer concentration whereas at higher polymer concentration, it was observed that the fiber diameter decreased significantly [155]. In another study using RSM, 8–10% polymer concentration with an applied voltage of 4–5 kV and tip to collector distance of 5–7 cm, aids in the development of silk fibroin nanofibers of less than 40 nm [156]. The pH indirectly influences the diameter of the fibers by affecting the concentration of the solution. Low pH decreases the polymer concentration, while gelation was observed at higher concentration which in turn reduces the average diameter of the fibers [157]. It is well understood that the mechanical properties of the fibers depend on the orientation and bonding which can be controlled by selecting suitable material and optimized processing parameters.

Generally, composite nanofibers are being developed to obtain an advantage over single polymer nanofibers. Addition of poly (ethylene oxide) (PEO) improved the processability by optimizing the viscosity and surface tension while no β-sheet structures were obtained. The crystallinity of the fibers was increased by treatment with methanol [158]. The co-related protein, silk sericin blended with silk fibroin, yields smooth and bead-free fibers with random coil and β sheet structure. The average diameter of the fibers as well as the water solubility were inversely related to the concentration of silk fibroin in the blend[159]. Regenerated composite fibers of silk fibroin and silk sericin were prepared by coaxial electrospinning type silk fibroin as the core and silk sericin aqueous solutions as the shell. The characterization study showed that the coaxially electrospun SF/SS fibers had more β-sheet conformation, better thermostability and mechanical properties than silk fibroin fibers alone due to dehydrating of fibroins by sericin which induced the conformational transition of fibroin to β-sheet structure [160]. In another study with core shell structure, poly (ε-caprolactone) (PCL) was used as shell material and heavy chain silk fibroin was taken as core material. Emulsion electrospinning was carried out to fabricate the blended nanofibers. The results of the study showed that ethanol treatment induced the formation of β-sheet in composite nanofibers, which improved the mechanical properties of blended nanofibers thus serving as suitable material for drug delivery [161]. Another bio-polymer blended with silk sericin to enhance the mechanical properties is cellulose acetate. Bead-free and smooth nanofibers were obtained by addition of 10% cellulose acetate to the polymer solution. Formation of crystalline fibers was facilitated due to the hydrogen bonds between the hydroxyl groups of cellulose acetate and the carboxyl and amino groups of silk fibroin [162]. Nanofibers with enhanced antibacterial properties against *Escherichia coli* and *Staphylococcus aureus* were prepared by blending chitosan with silk fibroin. The average diameter of the fibers was directly proportional to the concentration of silk fibroin whereas it was inversely proportional to the concentration of chitosan [163]. Improved bulk hydrophilicity, surface wettability, mass loss percentage, and decreased Young's modulus, tensile strength, and porosity was observed in the nonwoven version developed by blending gelatin with silk fibroin. This serves as an excellent carrier material for the antibacterial agents [164].

1.3.2.3 Bovine Serum Albumin

Bovine Serum Albumin (BSA) is described as a globular non-glycoprotein found predominantly in the circulatory system of the cow but is also a constituent of the whey component of bovine milk [165]. The molecular weight of BSA is close to 66430 g/mol, it is made up of 583 amino acid residues and has 17 cystine residues in three homologous domains [166]. BSA is generally economical and its biocompatible and stable nature make it an excellent candidate for electrospinning nanofibers [167]. However, the presence of strong intramolecular disulfide bridges makes it difficult for electrospinning. In this state, any solvent that disrupts the disulfide bridges could be used to make bead-free fibers. BSA nanofibers were generated from polymer solution containing different solvents, namely, aqueous medium, 2,2,2-trifluoroethanol (TFE), and in a TFE/beta-mercaptoethanol (β-ME). Aqueous solutions of BSA generated compact protein globules with a three-dimensional colloidal lattice structure. Protein unfolding was observed when TFE was used as solvent while disruption of intra-molecular disulfide bonds along with a higher degree of unfolding was observed in solutions prepared using TFE/β-ME. High extensional viscosity was observed in TFE/β-ME which prevented the breakage of the fibers into individual droplets, and resulted in a stable electrospinning process, producing continuous, smooth fibers [168]. Although formation of BSA nanofibers was achieved, it is still difficult to electrospin pure BSA nanofibers due to their compact globular shape and viscoelastic properties. In addition, BSA is mostly used in biotechnology, tissue engineering, cell lines and hence crosslinking with aldehydes like glutaraldehyde for the development of insoluble fibers with longer stability is restricted due to toxicity [167]. Hence, it is blended with other compatible polymers to overcome this disadvantage. For application in two-dimensional biosensors, naturally high soluble BSA protein was electrospun into insoluble fibrillar structures without altering the biological properties of BSA by blending it with PEO [169]. Another choice of polymer for blending with BSA is poly caprolactone) (PCL). Green electrospinning of BSA/PCL was achieved by preparing the polymer solution using formic acid and acetic acid (1:1 v/v) as a solvent. Improved elasticity and elongation were observed in blended fibers over pristine fibers [170]. The electrospun fibers to sustain the release of nerve growth factor (NGF) were fabricated by blending BSA and PCL. The developed fibers proved to be effective carriers and sustained release was observed over 28 days [171]. Emulsion electrospinning with core-shell morphology was developed by blending PVA and BSA. The key factors that influenced the formation of fibers were the blend ratio of PVA/BSA, molecular weight of BSA and applied voltage. It was found that the optimum ratio of PVA/BSA is 5:5 and the applied voltage of 22 kV has the better spinnability for the development of core–shell nanofiber structure [172]. This core shell structure was used as a carrier system for enzyme molecules such as acetylcholinesterase with good storage stability and better reusable stability [173].

1.3.2.4 Soy Protein Isolates

Soyabean is a widely cultivated legume in the world, and it contains the highest amount of protein content on a dry weight basis. Based on the protein concentrations from de-hulled and de-fatted soybeans, three types of protein products are processed, namely, soy flour, soy protein concentrates (SPC), and soy protein isolates (SPI) [174]. Among these, SPI is a globular protein containing the highest (85%–90%) protein content on a dry basis, mostly β-conglycinin with a molecular weight of 140–170 kDa and glycinin with a molecular weight of 340–375 kDa [175]. In the aqueous phase, these components exist as sphere molecules containing hydrophilic shells and hydrophobic cores [176]. Due to its biodegradability, non-toxicity, low cost, and abundant nature, SPI has gained popularity in biomaterial applications especially in food packaging and biomedical science.

The fabrication of pristine SPI nanofibers is highly challenging due to its globular structure. To facilitate the spinning process, SPI has to be denatured prior to electrospinning along with the addition of copolymer or carrier polymer [46,125]. Vega-Lugo *et al.,* (2008) was one of the first authors to report fabrication of SPI nanofibers by the process of electrospinning. In this study, along with PEO as carrier polymer, he used 1% NaOH and a surfactant (Triton X100) to facilitate the spinning process and developed e-spin nanofibers with an approximate fiber diameter of 240 nm. He reported that fibers with different morphologies can be prepared by altering the proportion of SPI and PEO [177]. In the following year, the same research group incorporated antimicrobial compounds in SPI composite nanofibers composed of SPI, PEO and PLA. Smooth bead-free fibers with diameters ranging from 200 nm to 2 μm were developed at an applied voltage of 20–30 kV with flow rate of 0.04 mL/min and in this study, fiber morphology was affected by the concentration of bioactive compounds that were incorporated [178]. In several studies, PEO was used as a carrier material to form SPI composite nanofibers [179] along with the addition of other bioactive compounds like red raspberry extract [180], lignin [181], and antimicrobial compounds [178,182]. Other copolymers blended with SPI for the fabrication of nanofibers is Polymide-6 (PA-6). 10 wt% of SPI prepared in aqueous acetic acid was blended with 45 wt% PA-6 prepared in formic acid solution and was subjected to electrospinning at various ratios. With the decreased amount of PA-6 in the ratio of SPI/PA6, the fiber diameter was gradually reduced, due to the decreasing viscosity of the spinning fluid. Silver nanoparticles were incorporated in the fibers to improve the antimicrobial activity [183]. Hybrid protein nanofibers were developed from the polymer solution prepared using SPI and PVA in distilled water. 11 wt% of polymers in equal ratios were spun into fibers but the SEM image revealed beaded fibers. Upon addition of Triton X as a surfactant, the surface tension of water was reduced and hence, smooth bead-free fibers were developed [184].

1.3.2.5 Whey Protein Isolates

Whey proteins are globular proteins which are derived during milk processing as a by-product during the cheese and casein production. Whey proteins contribute 20% of the total protein amount and are the second highest amount of protein in milk next to casein [185]. Due to its nutritional value, functional properties, and economical benefit, it is a widely accepted polymer for the use in food industry. The β-lactoglobulin (BLG) and α-lactalbumin (ALA), are predominant whey proteins with an isoelectric point of approximately 5.2 and 4.3, respectively [186]. Similar to other proteins, the globular structure and high electrical conductivity of the polymer solution tends to be challenging for the electrospinning of whey protein isolates (WPI) [125]. Hence addition of compatible polymers or the denaturation of protein can effectively aid in the production of WPI based nanofibers. The growth of nanofibers using PEO as a copolymer with WPI was studied. The denaturation of WPI was carried out at 85 °C for 30 min. Spin dope solution at various ratio (100:0, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80 and 0:100) was prepared by mixing 9 wt% PEO and 10 wt% WPI in distilled water. Smooth bead-free nanofibers with thermal stability up to 200ºC were obtained from the solution containing PEO concentration between 40% to 100% [187]. Similarly, PEO was used as the copolymer to blend with WPI for the fabrication of bead free ultrathin fibers [188,189]. Natural polymer blends were also investigated for blending with WPI. Pullulan, a linear polysaccharide carbohydrate polymer was blended with the protein, WPI. The effects of solution and process parameters were studied on the morphology of electrospun blended nanofibers. Increased viscosity and decreased conductivity were observed in the addition of pullulan to the polymer solution. In comparison, the influence of solution parameters governed the fiber development more than the process parameters. Improved thermal stability was also observed in the blended nanofibers than the pristine fibers [190]. A needleless electrospinning technique was used to prepare WPI and dextran nanofibers. Different molecular weights of dextran such as 40, 70, and 100 kDa in various ratios was blended with WPI to obtain the final solution concentration of 50 wt%. The study reported that both 70 and 100 kDa of dextran and WPI at mixing ratios of 2:1 and 3:1 in phosphate buffer (30 mM, pH 6.5) was found to be spinnable into nanofibers [191].

1.3.3 LIGNIN DERIVATIVES

In general, lignins are extracted as byproducts from the wood pulp, paper and lignocellulosic industries [192]. It is a polymer of propyl phenol units, namely, coniferyl alcohol and sinapyl alcohol, and *p*-coumaryl alcohol [193] with three-dimensional networks consisting of ether bonds as more than two-thirds of the linkages while the remaining are carbon–carbon bonds [194]. Pure lignin nanofibers were developed from the Alcell lignin by the process of electrospinning. With and without the addition of platinum, lignin nanofibers were produced from the polymer solution containing ethanol as a solvent. The spin dope solution of lignin was prepared in a 1:1 weight ratio of Alcell lignin and ethanol and with the addition of Pt, the solution was prepared in the ratio of lignin, ethanol, and platinum acetyl acetonate 1:1:0.002 and 1:1:0.004 on a weight basis. The solution was electrospun with 20–25 cm tip to-collector distance, applied voltage of 12 kV and flow rate between 0.06–0.8 mL/h. The developed nanofibers had diameter between 400 nm to 1 μm after carbonization [195]. Similarly, phosphorus functionalized lignin nanofibers were prepared in a single step electrospinning process. The spin dope solution was prepared in the ratio of 0.3:1:1 of H_3PO_4/Alcell lignin/ethanol and subjected to electrospinning. The fibers developed after carbonization resulted in submicron sized nanofibers [196]. Lignin composite fibers were developed by blending different types of lignin such as softwood and hardwood Kraft lignin, sulfonated Kraft lignin, and lignin sulfonate (LS) with PEO. DMF was used as solvent for the blend of softwood and hardwood Kraft lignin while water was used for the other types. It was found that without the copolymer, no fiber formation was observed in any kind of the lignin [197]. In another study, varying concentration of lignin (25 to 45 wt%) was added to PEO (0 to 0.2 wt%) using DMF as solvent. The solution, when spun into fibers possessed fiber diameters in the range of 443 nm to 3261 nm [198]. Lignin hybrid nanofibers were developed by blending with the thermoplastic polymer, PAN. The developed fibers from this blend were irradiated and crosslinked to enhance the thermal and mechanical properties of the nanofibers [199]. Another polymer used for the fabrication of lignin nanofibers is PVA. Softwood kraft lignin, PVA and cellulose nanocrystals were used in the study to develop composite lignin nanofibers. Here, cellulose nanocrystals were used as reinforcing agents. Various combination ratios of lignin, cellulose nanocrystals and PVA were prepared as the spin dope solutions and electrospun at 8 mL/min feed rate and applied voltage of 19 kV and the humidity was maintained between 35–45%. From the study it was concluded that PVA concentrations below 5% resulted in beaded fibers, and that the addition of cellulose nanocrystals lowered the degree of crystallinity and the melting point but increased the thermal stability of the composite nanofibers [200].

1.4 APPLICATION OF BIOPOLYMER-BASED NANOFIBERS

Nanofibers fabricated from the natural polymers are applied in various fields including but not limited to agriculture, food packaging, tissue engineering, filtration, drug delivery and sensors. In agriculture, encapsulation of agrochemical inputs such as fertilizers, pesticides, insecticides, bioinoculants, and pheromones are of major concern due to the impact of the external environment. The incorporation of a pheromone in nanofibers was used in insect management. Synthetic sex pheromones from the oriental fruit moth, *Grapholita molesta* (OFM) were successfully incorporated in the cellulose acetate nanofibers and slow release of pheromone was achieved over a period of up to three weeks [202]. Improved seed vigor, and enhanced seed germination was observed in seeds coated with nanofibers [203,204]. Cellulose acetate and gelatin nanofibers loaded with copper nanoparticles promoted seed germination even in the disease media condition [204]. The polarity of poorly water-soluble fungicide ‘Thiabendazole’ was improved by inclusion complexation with cyclodextrins nanofibers [205]. In another study, *Trichoderma viride* spores were successfully encapsulated in chitosan electrospun mats and it was found effective against diverse phytopathogenic strains including *Fusarium, Alternaria* [206].

Food packaging mainly focuses on maintaining the quality of products during production, transportation and storage and protecting it from physical, chemical, and biological degradation [207]. The quality, safety and shelf life of the produce is improved by the enormous development in active and intelligent packaging. Electrospun nanofibers are extensively applied in these techniques due to high fabrication rate and comparative low cost [208]. It is used in active packaging to enhance the shelf life of fruits by incorporating a bioactive volatile compound like hexanal in protein based nanofibers using zein [209]. In intelligent packaging system, nanofibers developed using chitosan [210], starch [211], bacterial cellulose [212], gelatin [213] are used in indicators and wheat gluten [214] nanofibers are used in sensors.

In tissue engineering, scaffolds fabricated using nanofibers are applied as they can be fabricated and molded according to the anatomical defects. Nanofibers are used in tissue/organ repair and regeneration, as carriers to deliver drugs and therapeutics, as medical implant devices, in medical diagnostics and instrumentation, as protective fabrics against environmental and infectious agents in hospitals and general surroundings, and in cosmetic and dental applications [208].Using core-shell nanofibers, sustained release of fluorescein-isothiocyanate-conjugated bovine serum albumin (FITC-BSA) was observed when cultured with human dermal fibroblasts (HDFs) [215].

The unique high surface area of the electrospun nanofibers has received massive attention in sensor applications. The conductometric sensors use this property to absorb more gas analytes which changes the sensors' conductivity accordingly and this also improves the sensitivity of the sensors. β-cyclodextrin has been introduced into a poly (methyl methacrylate) nanofiber membrane by a physical mixing method for the development of an affinity membrane to remove organic waste [216].

Green electrospinning is the concept used for the development of nanofibers from natural fibers which contributes to environmentally friendly and sustainable development. Pollution leads to negative health effects which can be mitigated by using nanofibers from biopolymers/natural polymers [217]. Nanofiber mats are used in various air filtration techniques either *per se* or with other filtration techniques to prevent pathogenic bacteria, viruses, particles, and other contamination in the environment. Similar to high-efficiency particulate air-filter (HEPA), electrospun nanofibers using gelatin were fabricated to efficiently remove particulate matter [218].

1.5 CONCLUSION

The demand for biodegradable polymers with unique topological, mechanical, and chemical properties is enormous and can be achieved by the fabrication of bio-polymeric nanofibers through the process of electrospinning. The development of ultrafine non-wovens using the polymers derived from bioresources have a wide range of applications as mentioned briefly above. Significant research has been conducted in this field to improve the properties of fabricated nanofibers to achieve the desired morphology. The properties include improving the solubility by adding suitable derivatives, using a mixed solvent system, incorporating copolymers to improve the solution properties such as viscosity, surface tension and conductivity or by the addition of crosslinkers. Most of the research carried out remains as research findings and will need up-scaling for commercial use. Despite the advancement in research on bio-polymer based nanofibers, the choices of the right polymer, the amount of bio-polymer to be used, the reduced use of toxic solvents, the size of nano fibers (woven/non-woven) for mass applications, and so on, is still required. More importantly, degradation studies and studies on the stability of the bio-polymeric fibers thus produced on a large-scale for cutting-edge applications needs to be analyzed along with their impact on environmental health.

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Morphology and Mechanical Properties of Epoxy/Synthetic/Natural Fiber Composites

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Bejoy Francis

Contents

Abstract

Epoxy resin is a widely used matrix materials for making composite materials. Natural as well as synthetic fibers are extensively used in composites. The use of synthetic fibers can be reduced by using natural fibers along with synthetic fibers. Natural fibers like hemp, flax, kenaf, jute, etc. have been used in conjunction with synthetic fibers like glass, Kevlar, and carbon. The ultimate properties are depen-

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9

Water Absorption Studies in Epoxy Nanocomposites

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9.1 Introduction

Epoxy resins are the most versatile among the thermosetting polymers. Since its commercialization in 1946, they are accepted as workhorse raw materials among the various thermosetting polymers. They are used as adhesives, coatings and matrices for composite materials in microelectronic industry, aerospace industry, etc. The cured resins are characterized by high chemical and corrosion resistance, good mechanical and thermal properties, low shrinkage upon cure, and flexibility in processing [1]. Despite all these characteristics, epoxy resins have low impact strength and fracture toughness. The fracture toughness can be improved by blending with elastomers or thermoplastics [2–4]. Similar to other materials, epoxy resins are also susceptible to moisture absorption, which in turn decreases their physical properties. The extent of water uptake depends on several factors like the number of hydroxyl groups, glass transition temperature, and the presence of other dispersed materials.

Nanotechnology has gained much interest in the last few decades [5]. The properties of epoxy resins are influenced by the addition of nanoparticles. Carbon nanotubes (CNTs), nanosilica, nanoclay, graphene, graphene oxide, TiO_2, etc. have been used extensively to modify epoxy resins [6–10]. Among these, the most widely used nanoparticle is clay and its modifications. Since epoxy resins are exposed to atmosphere in a large number of applications, the effect of moisture absorption on its properties is very crucial. Therefore, the research on moisture absorption behavior in epoxy resins arose much interest. The moisture absorption in epoxy resin can be affected by the type of resin used, the nanomaterial used, the conditions prevailing at the time of moisture absorption, etc.

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Chapter

23

Sars-Covid-2: Vaccines, Drug Repurposing, Global Health Security and Mental Well-Being

Renjith Thomas, Anila Skariah

Introduction

According to various findings, an unexplained outbreak of pneumonia in Wuhan, China, first occurred in December of 2019. Following the identification of a new corona virus that was determined to be responsible for the infection, it was named COVID SARS-2 and given the latter as the secondary designation of acute respiratory syndrome corona virus (SARS-CoV-2) (Lake, 2020). The WHO declared the crisis an international public health emergency on January 30 and a pandemic on March 11. As per the WHO database, COVID-19 has, so far, as of April 19, 2021, recorded over 140,886,773 instances resulting in 3,012,251 deaths and widespread social and economic impact. In the event of an epidemic of the primary treatments (specifically, vaccines) would have to be supplemented by non-specific supportive measures for people to have some hope of survival (Yuen et al., 2020).

These beta corona viruses have infected a third- of people worldwide and triggered two more recent or additional zoonotic outbreaks: SARS-CoV-1 (2002-2003) SARS-CoV-2 (2012 to the present) in the last two decades, plus MERS-CoV in the previous

decade. The presence of several SARS-related corona viruses and the appearance of SARS-related novel strains support the notion of zoonotic mechanisms. Since it is highly infectious, SARS-CoV2 usually spreads via respiratory droplets, through physical touch.. Social distancing from others, regular hand washing, and disinfecting surfaces can help prevent you from contracting infectious diseases.

Vaccine development against n-CoV-2

Researchers have attempted to create several vaccines for the COVID-19 pandemic. Most of these attempts have used the S-protein of SARS-CoV-2 (Ong et al., 2020). On the worldwide SARS-2 landscape, as of July 2, 2020, the number of candidates in the early phases of production includes 158. Analyzing mRNA-1273 (Moderna), Ad5-nCoV (Inovia), INO-4800 (Inovio), and Covisheild (Indian name) (Oxford University & Astrazeneca) is currently available in the market and are more effective and less expensive (Kaur & Gupta, 2020). Astrazeneca is a non-replicating viral vector vaccine like the Russian vaccine, but Pfizer and Moderna vaccines are mRNA based. New technologies that improve the immune system's immunogenicity, including AS03 (GSK), MF-59 (Novis), Cp1018 (Dynax), etc., are also under development. The immunoinformatics method is also being used for SARS-CoV-2 peptide recognition. It may help identify the cytotoxic antibody epitope and B cell epitope (Forni et al., 2021).

Drug repurposing for COVID-19 treatment

The word medicine repurposing is used to describe the process of new therapeutical applications for existing medicinal products. Often called 'repurposing' or 're-using,' the technique is widely regarded as cost-effective (Loucera et al., 2020). Since only a few medicines have total selectivity of action, many can work against other or new conditions. Outbreaks of new diseases, like COVID-19 constitute a significant healthcare system problem. Efficient pharmacological therapies are urgently needed in tension with a lack of time to discover new medicines (Wang et al., 2020).

CHAPTER 6

Nanostructured Molecularly Imprinted Polymers in Electrochemical Sensing

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Abstract: Molecular imprinted polymers (MIP) are one of the promising method in various research area in which artificial receptor sites of targeted molecule were fabricated on a polymer matrix. These polymers are analogues to naturally occuring antigen-antibody system. Due to its high recognition capabilty and structural specificity towards the target molecule, these kind of polymers exhibits wide variety of applications in various fileds. Among the temendous applications, MIPs in electrochemical sensing got much attention in recent years. Innovative developments in nanochemistry again improve its applications in electrochemical sensing. In this chapter, we detailed the significance of nanostructured MIP focusing on multiwalled carbon nanotubes as supporting material in elecrochemical sensing applications. It presents recent progresses associated to molecularly imprinted electrochemical sensors based multiwalled carbon nanotubes.

Keywords: Applications, Electrochemical sensor, Molecularly imprinted polymer, MWCNTs, Nanostructured MIP.

INTRODUCTION

Molecular imprinting technology is the most developing area of research in which artificial binding sites of target or template molecule were created on a polymer network. A typical molecular imprinting process involves the fabrication of a pre-organized complex of chosen template molecule and its complementary functional monomer followed by a crosslinking polymerization in the addition of a suitable initiator [1]. Subsequently, the extraction of a target molecule using suitable eluents, complementary cavities of template molecule remains as such in the poly-

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