REVIEW

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Electrospun Polymeric Nanofibers for Malaria Control: Advances in Slow-Release Mosquito Repellent Technology

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Dedicated to Prof Emeritus Walter Focke from the University of Pretoria, South Africa, for his immense contribution in applying Chemical and Materials Engineering knowledge in efforts to eradicate malaria in endemic regions.

The textile industry comprises technologies that transform synthetic or natural fibers into yarn, cloth, and felt for manufacturing clothing, upholstery, and household linens. The major public health threat in tropical and subtropical countries is mosquito-borne malaria. Nowadays, the demand for insect repellent-based textiles is continuously rising, as they are used for protection against diseases transmitted by mosquitoes. The present work reviews studies on the fabrication of insect repellent containing electrospun polymeric nanofibers as principal tools for protecting people against mosquito bites. Electrospinning technology is a remarkably facile technique for fabricating polymeric nanofiber devices. The technique is outlined and elucidated. The performance of insect repellent-based polymeric nanofibers against mosquitoes is carefully reported and comprehensively reviewed in-depth. Furthermore, the progress made on the mathematical modeling of the release rate of repellents through polymeric nanofiber devices is reviewed. The reviewed studies demonstrate that repellents can be released slowly from electrospun nanofibers, increasing the product's protection period against insects. The reviewed works suggest that electrospinning technology has led to an effective and facile methodology for fabricating functional nanofiber textiles with insect repellent. The reviewed studies showed that product-based repellents can be effective not only against malaria but also against other mosquito-borne diseases.

1. Introduction

In various countries, infectious diseases such as malaria, dengue, yellow fever, chikungunya, and Zika virus are transmitted by mosquitoes.[1–6] The World Health Organization (WHO) has recommended several intervention methods, such as the treatment of malaria using Artemisinin Combination Therapy (ACT) drugs and vector control through the large-scale distribution of Long-Lasting Impregnated Net (LLINs) and Indoor Residual Spraying (IRS).[3] However, malaria remains the principal cause of hospital consultations in tropical and subtropical endemic regions, particularly in sub-Sahara Africa, which contributes to the high number of mortalities.[1,3] According to the latest WHO report, in 2021, ≈247 million malaria cases were reported, with an estimated number of 61 900 mortalities.[1] Most of the reported cases include children younger than 5 years and pregnant women who are considered most susceptible to malaria.[1,4–8] During that year, the WHO reported that ≈76% of the total

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number of fatalities were children.[1] The practical intervention methods mentioned above have been demonstrated to be effective in indoor environments and not in outdoor environments, where people are more likely to be bitten by mosquitoes due to the long period of time that they spend during the day and early evening.

Safe personal protection against mosquito bites using wearable-insect repellent devices has been considered as a suitable practice to reduce the transmission of various diseases by mosquitoes to people.[2–4,9–12] Insect repellents are volatile chemicals that repel away insects (i.e., mosquitoes) when applied on human skin. Thus, as a result, the insect repellents discourage contact and insect bites on humans.[4,5,13–15] There has been increased interest in studies on the control of pests using insect repellents derived from plants due to their low toxicity and environmental friendliness.[6,16–18] However, due to their high volatility, these plant-based insect repellents have been shown to have shorter periods in which their repellence activity is sustained.[2,19–23] Icaridin, ethyl anthranilate, ethyl butylacetylaminopropionate (IR3535), and *N, N*-diethyl-m-toluamide (DEET) have been proposed as promising candidate insect repellents to replace insecticides due to their low toxicity compared to insecticides.[1,2,24–31] Various products-based insect repellents, including creams, roll-ons, and sprays, are commercially available to protect people against mosquito bites indoors and outdoors. The principal concern with their use is related to their short period of protection when applied on the skin of humans, where most of them only provide protection for a few hours.[5,32–36] These products-based insect repellents involve topical skin use, and need recurrent use due to environmental situations, including excessive sweating, humidity, and mosquito activity. As a result, presently the application of product-based repellents necessitates recurrent application, and their wide-scale use would not be reasonable or accessible to poorer societies. Extended periods of protection against mosquito bites are therefore necessary and mandatory.

Fabrics with repellent activity have been previously developed by using different procedures, such as polymer coating, microencapsulation, and inclusion of repellents in cyclodextrins grafted to textiles.[7,37–40] Electrospinning provides a versatile technology to fabricate three-dimensional nanofibrous non-woven mats using various materials with fiber diameters ranging from micro to nanoscale, depending on the material properties and processing conditions employed to fabricate the nanofibers.[8,41–47]

In recent years, electrospun mats have been proposed for various bio/nanotechnological applications due to their attractive structural, morphological, and functional characteristics.[8,9,48–50] In addition, electrospinning polymeric materials have been demonstrated to be effective in drug delivery and in prolonging the insect-repellent release.[10–17,51,52] The produced polymeric fibers can be tested for their composition and repellent release rate.[14–16] For example, Ryan et al.[14] showed that monofilament nylon polymeric nanofibers extended the release rate of DEET with a time of 70 h. The insect-repellent Picaridin was also used to produce polymeric nanofibers, and it was confirmed that the fibers prolonged the release rate of the repellent.

Furthermore, a range of materials are applied in electrospinning. A study done by Muñoz et al.[2] produced insect-repellent-containing electrospun ethyl cellulose nanofibrous mats via the electrospinning technique for the control of disease vectors. The results demonstrated that applying biopolymer-based core-enriched nanofibrous mats resulted in a promising strategy for developing functional nanofibrous textiles containing natural repellent cargo, such as disposable outdoor goods. Biodegradable electrospun polymeric nanofibers have also been prepared using poly(L-lactic acid) (PLLA) containing DEET.[17–24,53]

Although there is an abundance of extensively reviewed literature on electrospun fibers for several applications, none focuses on electrospun nanofibers-based mosquito repellents. Hence, the current review focuses on the use of electrospinning technology in the fabrication of nanofibers-based mosquito repellents. **Table 1** shows descriptions and qualitative analysis between the current and previously published reviews. The previous reviews offered limited insight on the basic principles of the fabrication of nanofiber-repellents using the electrospinning technique and the characterization of the nanofibers-repellents systems. The closest attempt to the current work was the review by Khalf and Madihally.[54] However, this present study is more concise and aims to provide a more heuristic understanding of electrospun nanofibers-based insect repellent devices produced by electrospinning as a new tool for controlling infectious diseases (i.e., malaria) in endemic regions. In this study, techniques such as scanning electron microscopy (SEM) and confocal Raman spectroscopy are used as a characterization basis for understanding the morphological and chemical structure (the interaction between polymer and repellent) properties of the electrospun nanofibers-based insect repellent devices.

To the best of our knowledge, reviews on the development of electrospun polymeric nanofibers-based repellents, and their repellency activity are yet reported upon, thus prompting this work. In this paper, a review of electrospun nanofibers used in repellent delivery for mosquito bite control is conducted with respect to i) fabrication of nanofibers by electrospinning technique; ii) Mechanism of repellents release from the electrospun polymeric nanofibers; iii) the effectiveness of repellent-based electrospun polymeric nanofibers against mosquito bites; and iv) mathematical models for the release rate of repellents though electrospun polymeric nanofibers. Furthermore, challenges and future perspectives are also addressed.

2. Fabrication of Nanofibers by Electrospinning Techniques

The origins of nanofiber fabrication trace back to Charles Vernon Boys' pioneering work in 1887, while John Francis Cooley obtained the first patent in 1900, marking the early milestones in this field.[59] The exploration of fluid behavior under electrostatic forces subsequently led to the development of mathematical models. The period between 1931 and 1944 witnessed the golden years of electrospinning technology, marked by Anton Formhals' prolific patent submissions, amounting to nearly 22 patents.[59] The initial attempts at crafting electrospun nanofibrous filters can be traced back to 1938. It was not until the early 1990s that the term "electrospinning" gained popularity, marking the inception of a new era for this technology.[59] Since then, there has been an exponential increase in scientific publications and technical reports concerning nanofibers and electrospinning technology.

Table 1. Review articles on electrospinning technology and their applications previously published in the literature compared to the present work.

References	Main goal
[54]	This review describes the recent advances in the controlled drug release from multiaxial electrospun fibers in drug delivery and tissue regeneration applications, including the influence of fiber properties on performance for example, fiber size orientation influence the immune system's activation, similar to stem cell differentiation. They also focused on the modeling of the drug release.
[55]	This review focuses on the applicability of nanofibers incorporated with drugs or drug nanoparticles in managing diseases, especially on disorders related to the brain, eye, ear, cardiovascular system, lungs, and oral cavity. They also extended their review to reporting on the use of nanofiber-based drugs in diseases with higher mortality rates, such as diabetes.
[56]	This review summarizes current strategies focused on the development of advanced nanofibrous polymer-based scaffolds using electrospinning, their applications in regenerating human musculoskeletal tissues, and polymer nanofibers to deliver growth factors or small molecules for regenerative medicine.
[57]	The review intends to bridge the gap between the dissolution properties of drug-loaded fibers containing either small molecules or macromolecules and the characteristics of fibrous formulations. The authors highlighted the various formulation possibilities offered by nanofibrous delivery systems due to their unique microstructure, which enables the formulation of tunable matrices for various drug loadings. The focus of the drug delivery targeted regenerative medicine.
[58]	The main aim of this review is to summarize the basic principles of electrospinning as well as the most recent developments regarding biomedical engineering, focusing on drug delivery. In this review, the application of drug delivery-based nanofibers is in the field of regenerative medicine.
Present review	The present review describes the electrospinning technology and its applicability in fabricating electrospun polymer nanofibers-based mosquito repellent. The applicability of mosquito repellent as drug incorporated nanofibers in managing infectious diseases, particularly malaria transmitted by mosquito bites, is also described. The use of SEM and Confocal Raman spectroscopy to characterize the morphology and structure of nanofibers-based insect repellents is reported. It also explains how these new strategies or tools can contribute to reducing malaria in endemic regions. Studies reporting on insect-repellent-based nanofibers' repellency activity against mosquito bites are also reviewed.

While a standard definition limits nanofibers to fibers with diameters up to 100 nm, the textile industry often extends this range to encompass fibers with diameters up to 1000 nm.[60] Nanofibers, characterized by their remarkable properties, including high porosity, large specific surface area, small pore size with a narrow distribution, and a wide range of available diameters (40–1000 nm), have found applications in various technological and commercial domains.[60] These include air filtration, medical and healthcare products, batteries, oil–water separation, and membrane separation technology, among others. Nanofibers can be crafted from an extensive array of natural and synthetic polymers.[61,62]

A typical electrospinning setup comprises four core components: a high-voltage supply, a dope injection system (usually a syringe pump), a needle or spinneret, and a grounded, conductive collector.[63] The process begins with the formation of a pendant droplet as the dope solution is injected into the needle. Upon the application of a direct current electric field, this droplet transforms into the iconic Taylor cone. When a high voltage is imposed, the electrostatic charge overcomes the surface tension of the dope solution, resulting in the ejection of a single nanofiber from the Taylor cone.[63,64] The formation, shape, and trajectory of the charged solution jet between the needle tip (Taylor cone) and the collector are influenced by several parameters, including the applied electric field, conductivity of the dope solution, dope flow rate, viscosity, surface tension of the dope solution, needle gauge, and the distance between the spinneret and the collector.[65,66] **Figure 1a** shows an illustrative electrospinning schematic.

The electrospinning technique presents multiple advantages for membrane fabrication compared to conventional methods.[62,67] It accommodates various polymers and inorganic materials, making it suitable for diverse applications. Electrospun nanofibers, known for their porous structure and high surface area-to-volume ratio, are particularly appealing for applications where highly porous membranes are essential, such as microfiltration and membrane distillation.[65] Additionally, the versatility of electrospinning enables fiber deposition on various substrates, including metal, nonwoven mats, and commercial membranes.[66] Furthermore, electrospun nanofibers can be readily functionalized through straightforward processes, such as blending different polymers for enhanced mechanical strength or post-electrospinning treatments. These advantages position the electrospinning technique as a cost-effective solution for laboratory-scale membrane production, and it can also prove more efficient and economical for large-scale applications.[62,66] Notably, it reduces polymer and chemical/toxic solvent usage compared to conventional membrane manufacturing methods.

3. Classification of Electrospinning Methods Based on Design

3.1. Melt Electrospinning

Traditional electrospinning relies on polymers that can be dissolved in solvents, limiting its applicability to membrane production.[68] To address these limitations and embrace a more sustainable approach, the method of melting electrospinning has emerged. In this process, a molten polymer creates ultrafine nanofibers, eliminating the need for hazardous solvents and enhancing safety. This results in reduced manufacturing costs and increased efficiency compared to the conventional electrospinning method.[69,70] However, the energy required for polymer melting makes this process more energy-intensive.

A visual representation of a melt electrospinning setup is depicted in Figure 1b. The molten polymer is stored in the supply zone and transported to a capillary (spinneret) through various means, such as a plunger pump or air pressure.[69,70] As the molten polymer is expelled from the spinneret, a high electri-

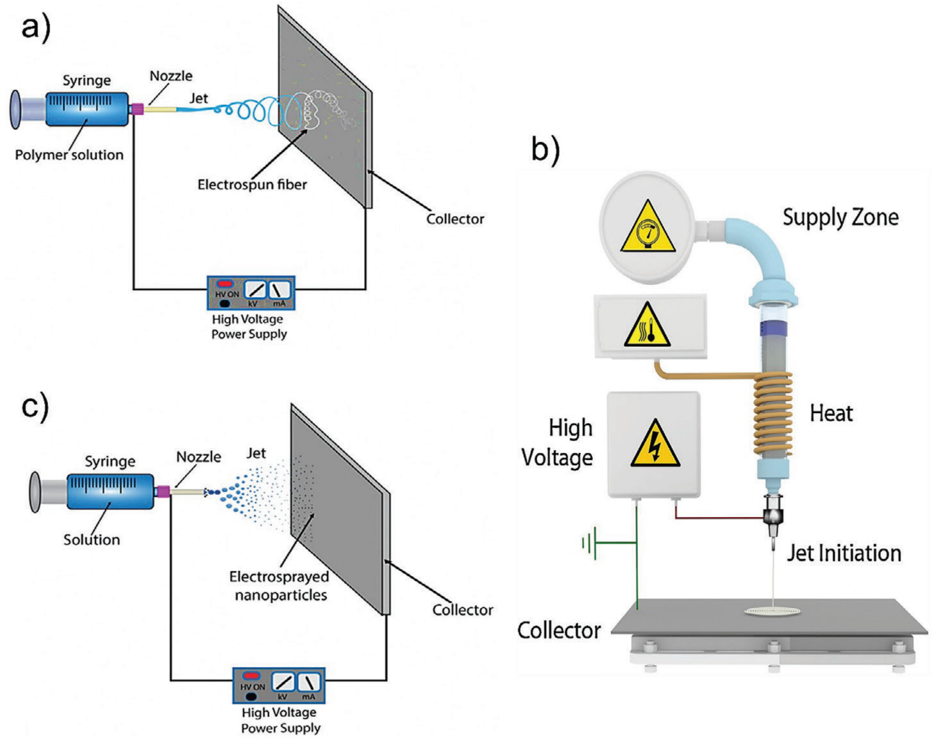

Figure 1. Illustrative diagram of different electrospinning systems. a) Conventional electrospinning. Reproduced with permission.[74] Copyright 2021, Elsevier. b) Melt electrospinning. Reproduced (Adapted) with permission.[75] Copyright 2016, Elsevier. c) Electrospraying. Reproduced with (Adapted) permission.[74] Copyright 2021, Elsevier.

cal potential is applied between the molten polymer and the collector surface, leading to the development of electrical charges on the surface of the molten meniscus.[69,70] The increased electrical charges on the molten polymer result in repulsive interactions known as repulsive Coulombic forces.[69,70] These forces compete with the surface tension of the molten polymer, which encourages spherical shapes and smaller surface areas, causing the droplet to deform.[69,70] When the repulsive Coulombic forces overcome the surface tension of the droplet, a conical shape referred to as the "Taylor cone" is formed.[69] An electrostatically charged jet is drawn from the Taylor cone toward the collector surface by surpassing the critical velocity of the fluid, leading to the solidification of ultrafine filaments.[69]

The melt electrospinning system typically comprises a polymer melt supply zone, a spinneret, and a fiber collection zone. To introduce a polymer into the melt electrospinning process, polymer materials are typically loaded into a syringe, which can be made of plastic, metal, or glass.[70–72] The polymer in the syringe is preheated to eliminate any air pockets and ensure a continuous polymer supply into the system.[69,73] Subsequently, the syringe is placed in a heating jacket to maintain the molten polymer at a constant temperature.[69] The temperature of the polymer is raised slightly above its melting point to facilitate its flow and minimize thermal degradation.[69,73]

Typically, a syringe pump is employed to regulate the extrusion of the polymer melt from the syringe or the custom heating chamber.[69] In most melt electrospinning systems, an electroconductive spinneret connected to the syringe or the custom heating chamber is used to extrude the polymer melt. The spinneret is usually a flat-tipped hypodermic needle with a circular cross-section. An additional heater can be used to heat the spinneret independently. The heating of the spinneret aims to lower the melted viscosity, ensuring a smooth flow through the narrow-diameter spinneret and preventing the solidification of the Taylor cone near the spinneret.[69,76,77] Generally, the metallic spinneret is connected to a high-voltage source, while the conductive surface serving as the fiber collector is either electrically grounded or oppositely charged.[69] In most melt electrospinning setups, the fiber collector is positioned directly under the spinneret, and the molten jet flows downward directly towards the collector. Consequently, the influence of gravity on the jet flow is negligible compared to the applied electrostatic forces.[69,73] Various metallic surfaces, including aluminum, stainless steel, copper plates, glass, or aluminum foil-wrapped plates, can facilitate the straightforward collection of fibers.[69,78]

3.2. Electrospraying

Figure 1c illustrates a typical configuration for electrospraying. In this process, fluid is introduced into a nozzle via a syringe pump. A high-voltage electric field is then established between the nozzle and a ground electrode positioned below it. Without applying voltage, the nozzle emits larger droplets. As the voltage is gradually increased, the drop at the nozzle's exit becomes polarized due to the electric field.[79,80] The interplay between electrical and hydrodynamic forces results in meniscus deformation. With further voltage escalation, the droplets take on a conical shape, and a fine jet emanates from the apex. Eventually, the jet breaks into finer droplets. As the solvents in each droplet evaporate, their size decreases, leading to the repulsion of any particles generated. These particles are collected either on the collector or the ground electrode.[79–81]

To ensure efficient solvent evaporation within the optimal distance between the electrode and nozzle and the required electric field magnitude for fluid atomization, determining the proper separation between the electrode and nozzle is crucial to this process. Different electrode shapes, such as annular electrodes (positioned several millimeters to tens of millimeters beneath the nozzle) and large surface area electrodes (typically several centimeters below the nozzles), have been employed in numerous studies. Regarding particle collection, some researchers have gathered them on ground electrodes, while others have employed dishes, often using a ring-shaped electrode placed in a dish beneath the main electrode.[79–82]

Electrospraying depends on a multitude of variables, which can be classified into three main categories: solution parameters, process parameters, and ambient parameters. Solution parameters encompass the physical characteristics of the liquid or solution, such as viscosity, conductivity, polymer molecular weight, and surface tension.[79–82] Process parameters include the applied voltage, flow rate, and geometrical aspects, including the distance between the nozzle and electrode. Ambient parameters involve the temperature and humidity of the surrounding environment. Electrospray-generated particles can find utility in surface modification of membranes.[79–82] Consequently, a comprehensive understanding of the critical parameters influencing the electrospraying process is indispensable for optimizing the desired product features.

3.3. Multi-Needle Electrospinning

Multi-needle electrospinning represents an evolutionary step beyond the conventional single-needle electrospinning method, employing an array of needles organized according to a specific configuration to execute the electrospinning procedure. The fundamental objective of multi-needle electrospinning is to augment the count of polymer jets generated by elevating the number of needles, thereby amplifying the yield of nanofibers. Nevertheless, the successful realization of multi-needle electrospinning technology is dependent upon fulfilling specific prerequisites, as the augmentation in needle quantity concurrently elevates the complexity of the electrospinning apparatus.[83] Two primary considerations must be considered when implementing multi-needle electrospinning.[83,84] First, it is imperative to ensure the consistent conveyance of the solution to each needle under a uniform pressure or flow rate, facilitating the continuous and even formation of the Taylor cone. Second, the electric field strength at the apex of each needle must reach a level adequate to surmount the surface tension of the spinning solution.[83]

3.4. Needleless Electrospinning

Nanofiber production via electrospinning can be accomplished using either a needle as the spinneret (known as needle electrospinning) or without a needle (referred to as needleless electrospinning). While needle electrospinning offers simplicity in laboratory settings, it comes with inherent challenges, including needle clogging and limited production speed. In response to these limitations, needleless electrospinning has emerged as an attractive alternative for large-scale nanofiber production, exhibiting satisfactory production rates and desirable physical and mechanical properties.[84]

Needleless electrospinning first surfaced in the early 1970s as a method for directly generating nanofibers from a liquid's open surface by concurrently forming multiple jets. This technique offers cost-effective processing and an efficient means of scaling up production. However, it is not without its challenges, particularly in terms of process control, as the formation of the primary jet in needleless electrospinning is a self-assembled process involving several distinct stages: i) The initial step involves creating a thin layer of polymer solution on the spinneret's surface; ii) Subsequent turbulence and excitation of this soluble layer lead to conical spikes; iii) By applying a high voltage, a Taylor cone is formed, concentrating electrical forces at the spikes and intensifying the excitement; iv) The culmination of this process results in jet formation and, ultimately, the production of nanofibers.[85,86]

Spinnerets, in the context of needleless electrospinning, assume a pivotal role in nanofiber production (**Figure 2**). Operational parameters such as the spinneret's shape, size, and rotational speed provide control over the nanofiber properties. The spinneret setup for needleless electrospinning can be broadly categorized into two main groups: i) Stationary spinnerets, where auxiliary forces like magnetic fields, gravity, and gas bubbles are often employed to initiate the electrospinning process; ii) Rotating spinnerets induce initial mechanical vibrations and create turbulence in the polymer solution, subsequently leading to the formation of starting jets. These types of spinnerets operate continuously.[86]

3.5. Blow Electrospinning

Electro-blow spinning represents a modified approach derived from electrostatic spinning. The adaptation involves incorporating a continuous airflow around the spinning nozzle, intensifying the fiber formation process. In its initial phase, the formation of fibers benefits from the tangential forces exerted by the circulating air, complementing the effects of the applied electrostatic forces. Subsequently, the flowing air swiftly removes solvent vapors from the developing fibers, significantly expediting solvent evaporation. Consequently, the introduction of airflow enhances the stability and efficiency of the spinning process. Moreover, specific characteristics of the resulting fibers, such as their diameters and quality, can be fine-tuned by adjusting parameters related to the flowing air, including air velocity.[88–91]

Researchers have coined various terms to describe this method, wherein fibers are created through the collaborative influence of electrostatic forces and the mechanical tangential effects of flowing air. These terms include blowing-assisted electrospinning, electro-gasodynamic injection, and gas-jet electrospinning. However, the term "electroblowing" initially used in a patent description (US73 90 452), has become the most widely accepted nomenclature. This compound term electroblowing clev-

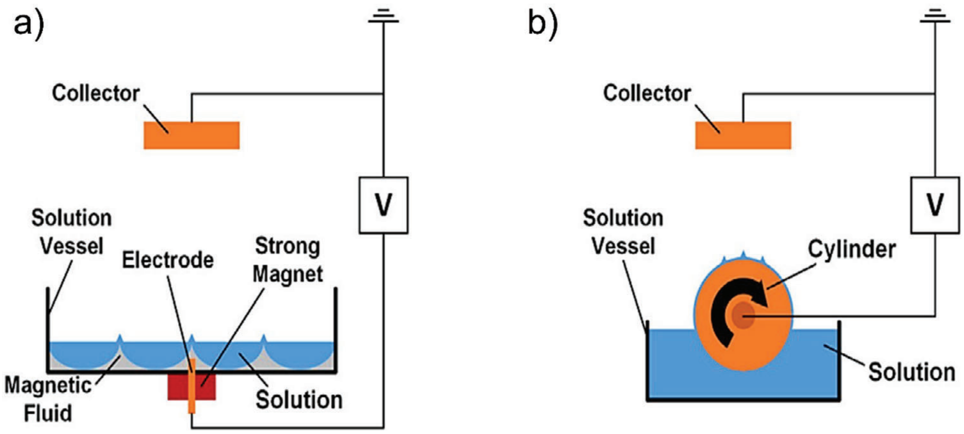

Figure 2. Illustrative diagram of needleless electrospinning. a) Rather than employing needles, a multitude of static, pointed, conical structures are formed within the polymer solution reservoir using a magnetic fluid as a template. b) The simultaneous formation of multiple sharp conical tips occurs because of the rapid rotation of a coarse cylinder. In the process of needleless electrospinning, a robust electric field is generated in proximity to each of these sharp conical tips when subjected to high voltage, causing the extraction of nanofibers from each of these tips. Reproduced (Adapted) with permission.[87] Copyright 2018, De Gruyter.

erly combines elements of “electrostatic spinning” and “solution blowing”.[88–92] Numerous researchers have further refined this innovative method by modifying and expanding upon one of the techniques mentioned earlier. One distinguishing feature between the original and the modified methods is the distance between the spinning nozzle and the collector electrode. In conventional electrospinning, this distance typically falls within the range of 10–20 cm, whereas in solution blowing, it extends from 80 to 100 cm.[88–91]

Figure 1a illustrates the schematic of the basic setup traditionally used for classic electrostatic spinning. In this setup, fibers are produced from a polymer solution, extruded from a capillary spinning needle. A high-voltage source is connected between the needle and the collector electrode. The electroblowing configuration depicted in **Figure 3** shares the same fundamental layout but incorporates an additional component: a source of flowing air, which is directed along the spinning nozzle via an air jet. The source of airflow and the air jet are the key elements that distinguish between the basic systems configurations of the two spinning methods.[88–92]

3.6. Coaxial Electrospinning Technique

Polymer nanofibers have garnered substantial interest over the past decade due to their remarkable attributes, including a high surface area-to-volume ratio and customizable chemical and physical properties across varying length scales.[94] A particularly intriguing development is the creation of core-shell or hollow nanofibrous structures from polymer solutions through the innovative coaxial electrospinning method (**Figure 4**).[95,96] This groundbreaking technique was initially introduced in 2002 as a swift, efficient, and meticulously controlled process, where multiple polymer solutions are individually dispensed via a coaxial nozzle and drawn to produce core-shell nanofibers.[97,98] Notably, this method has facilitated the fabrication of nanofibers with diverse materials and unique morphologies.[95,99] Core–shell nanofibers have applications in cargo delivery systems, mainly by providing protective layers for biologics within the inner layers. This safeguarding strategy prevents the deterioration of unstable components, such as growth factors and drugs, in reactive environments while enabling controlled release.[94,99] Coaxial electrospinning offers additional advantages, including the ability to fine-tune mechanical properties, degradability, good thermal and electrochemical properties, biocompatibility, and hydrophilicity through the judicious selection of core and shell materials.[95,96,99]

3.6.1. Core–Shell Structures

In the realm of core-shell structures, coaxial electrospinning is a widely employed method for generating these nanofibers, endowing them with enhanced mechanical properties, the potential for encapsulating and releasing macromolecules, and the versatility to achieve diverse morphologies.[95,96] Various techniques are used to fabricate electrospun porous fibers, including using volatile solvents like dichloromethane, humidity-based approaches, and collector immersion in water. Furthermore, introducing a low-surface tension core or shell can induce the controlled formation of highly porous fibers through interface instability.[95,101,102]

3.6.2. Hollow Structures

Hollow nanofibers, boasting their substantial surface area-to-volume ratios and material encapsulation capabilities, find applications in drug release, environmental protection, purification, separation, catalysis, sensors, gas storage, and energy conversion. Typically, coaxially electrospun hollow fibers are created through core elimination or dissolution (Figure 4c). It can be achieved via core-decomposition methods involving heat treatment or core-extraction methods, which rely on solvents. Both methods have certain limitations associated with

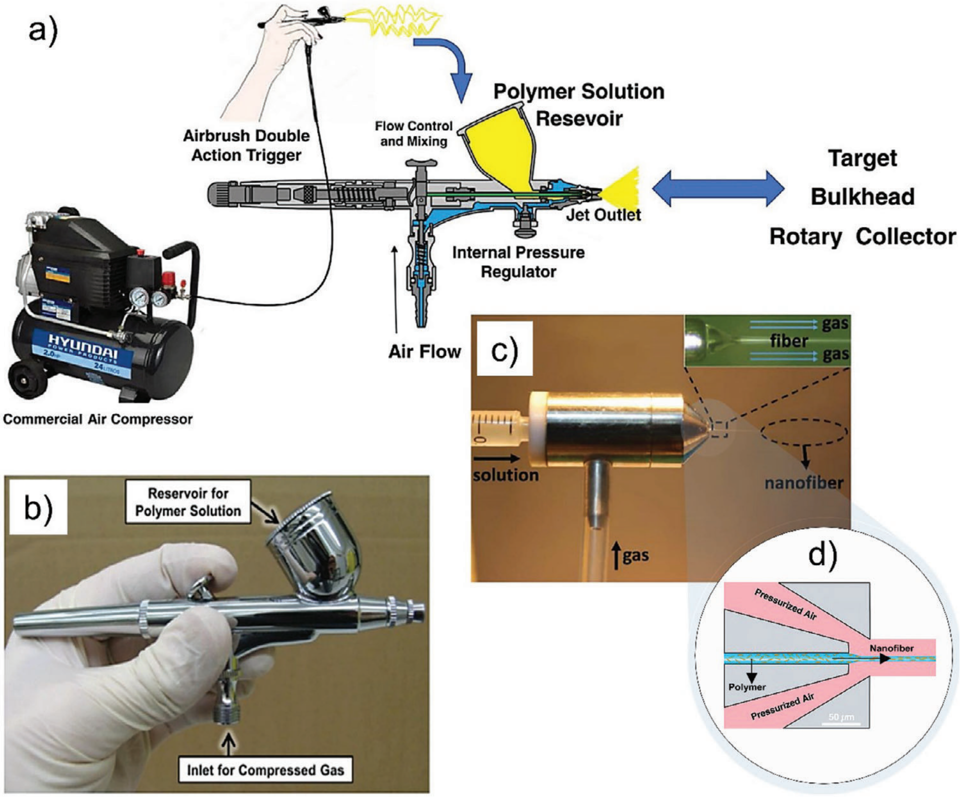

Figure 3. Schematic illustration of the basic setup traditionally used for classic electrostatic spinning Blow electrospinning: a) Illustrative representation of a commercial airbrush. b) A real commercial airbrush. c) Airbrush details. d) Schematic illustration of the simultaneous ejection of compressed air with the polymer. The polymer is crushed by the air forced through the exit hole, promoting the production of thinner nanofibers. Reproduced (Adapted) with permission.[93] Copyright 2020, Elsevier.

selecting shell and core polymers. The core-extraction method selectively dissolves the core materials while preserving the shell's structural integrity. In contrast, the core-decomposition method removes the core materials through heat treatment while maintaining the shell's stability. The core-decomposition method offers high reproducibility and the potential for uniform shell thickness and pore size. The functionalities of hollow nanofibers can be enhanced by modifying the surfaces, both inner and outer, with the incorporation of functional materials. The creation of porous hollow fibers is also feasible through the manipulation of polymer solution miscibility.[97,98,103,104]

3.6.3. Multichannel Structures

Multichannel structures which exhibit a complex design, are crafted through multifluidic electrospinning, followed by removing intermediate layers (Figure 4e). These multichannel nanofibers possess various advantages, including independent channels, substantial surface area-to-volume ratios, integration of multiple components/functions, and lightweight properties. Consequently, they have found utility in catalysis, energy storage, and drug delivery. The distinct attributes of each layer can be separately tailored to adjust mechanical properties, biocompatibility, hydrophilicity, electrical conductivity, and electrochemical activities. Multichannel configurations can be created by eliminating the initially incorporated multicores within the nanofibers.[97,98]

3.7. Bubble Electrospinning

Despite the success achieved by using electrospinning for nanofiber production, its limitations, such as low productivity averaging around 0.3 grams per hour per needle, have considerably restricted its wide scale industrial application.[105] These challenges have spurred researchers to explore alternative technologies. One promising avenue is bubble electrospinning, a method designed for the mass production of nanofibers. The concept has evolved into the mature Bubbfil spinning approach, encompassing variants like bubble electrospinning, blown bubble electrospinning, and more.[106,107] Bubble electrospinning, in particular, offers a straightforward means of fabricating a diverse array of nanomaterials, including nanoparticles, nanofibers, nano-yarns, nanoscale porous fibers, and others.[108] The process involves the generation of bubbles from a spun solution or melt, followed by the application of external forces (e.g., electrostatic force, centrifugal force, blowing air, vacuum receptors, hot or vibrating nozzles, and more) to rupture the bubbles. Subsequently, the resulting fragments hurtle towards a collector at exceedingly high velocities. Due to solvent vaporization and elongation induced

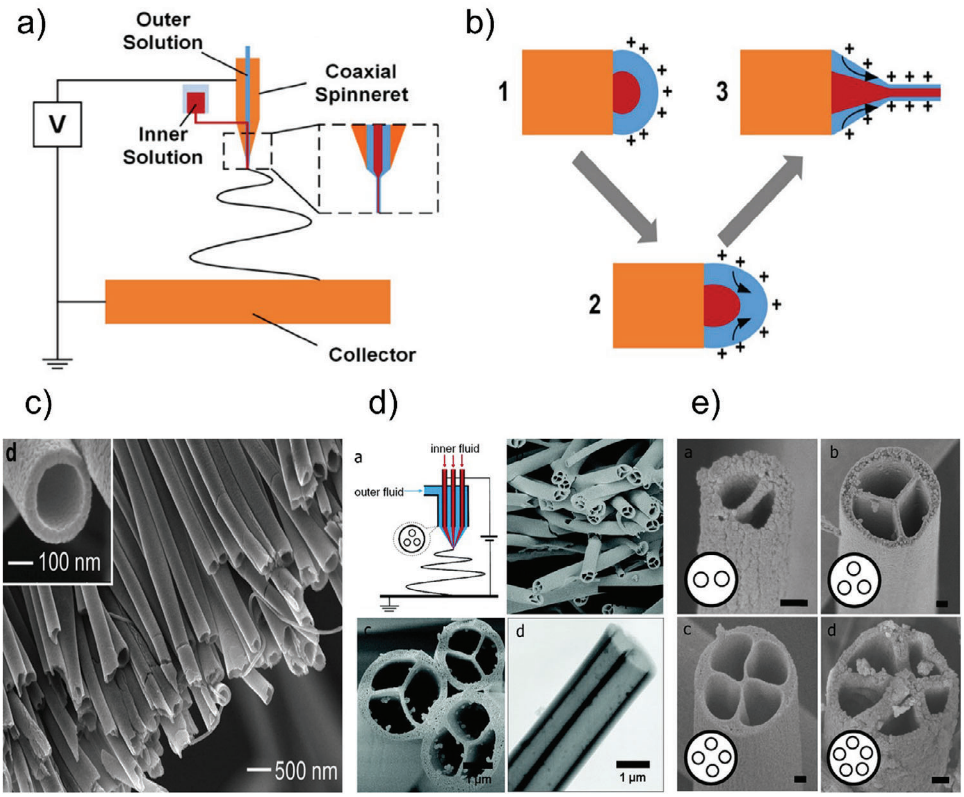

Figure 4. Schematic illustration of coaxial electrospinning. a) The nanofiber is formed from two different solutions through the internal and external channels. b) A Tylor cone is formed at the tip of the spinneret when a high voltage is applied between the spinneret and the collector. When stretched, the two-component solution forms core-shell nanofibers. c) SEM image of a hollow core nanofiber. Reproduced (Adapted) with permission.[87] Copyright 2018, De Gruyter. d) SEM image of a three-channel nanofiber; e) SEM images of multichannel nanofibers. Reproduced (Adapted) with permission.[100] Copyright 2007, ACS.

by air drag, these moving fragments progressively solidify into nanofibers.

For thousands of years, nature has bestowed spiders with the remarkable ability to spin silk. Spider silk possesses exceptional qualities, including remarkable flexibility, high strength (at least five times that of steel), lightness, extraordinary toughness, and elasticity.[109] While extensive research has delved into the genetic sequencing of spiders, the underlying mechanisms of spider silk production remain a mystery.[110] Revealing the enigma behind spider silk formation could catalyze advancements in synthetic fibers. One potential explanation lies in the exploitation of nanoeffects in bubble dynamics. The posterior portion of a spider's abdomen harbors numerous spinnerets, each composed of millions of nanoscale tubes (**Figure** 5a).[111] During the spider's silk-spinning process, a minute bubble emerges at the apex of each nanotube. Thanks to the remarkably low surface tension of these bubbles, spiders can effortlessly fashion them into nanofibers using their body weight or the tension generated by their hind legs. In essence, spiders can produce nanofibers with minimal effort. This analysis posits that a bubble measuring approximately 20 nanometers in diameter can form at the top of each nanotube.[111] The minuscule bubble's exceedingly low surface tension can be readily overcome by the tension generated by the spider's weight or hind legs.

Inspired by the spider's silk-spinning mechanism, bubble electrospinning was introduced in 2006 as a potential solution to the limitations encountered by traditional electrospinning methods. He et al.[111] presented a novel spinning technology to overcome the bottlenecks inherent in current electrospinning techniques. The initial bubble electrospinning system comprised four key components: a vertical solution reservoir, a bubble generator, a collector positioned above the reservoir, and a high-voltage power supply (Figure 5c).[112] A gas tube introduced at the reservoir's base facilitated bubble generation, with a fixed metal electrode running along the tube. It was observed that when a high voltage was applied, multiple small bubbles of varying sizes formed on the solution's surface. As an electric field was introduced, charges were induced onto the bubble's surface. Under the tangential stress resulting from the coupling of surface charge and the external electric field, the bubble underwent deformation, leading to the emergence of an upward-directed reentrant jet. As the electric field force exceeded the critical threshold required to overcome the bubble's surface tension, countless charged jets took shape on the conical bubble's surface. These charged fluid jets underwent stretching and refinement under the influence of the electric field force. Notably, the threshold voltage needed to overcome the bubble's surface tension is influenced by the bubble's size and air pressure. The most appealing aspect of bubble

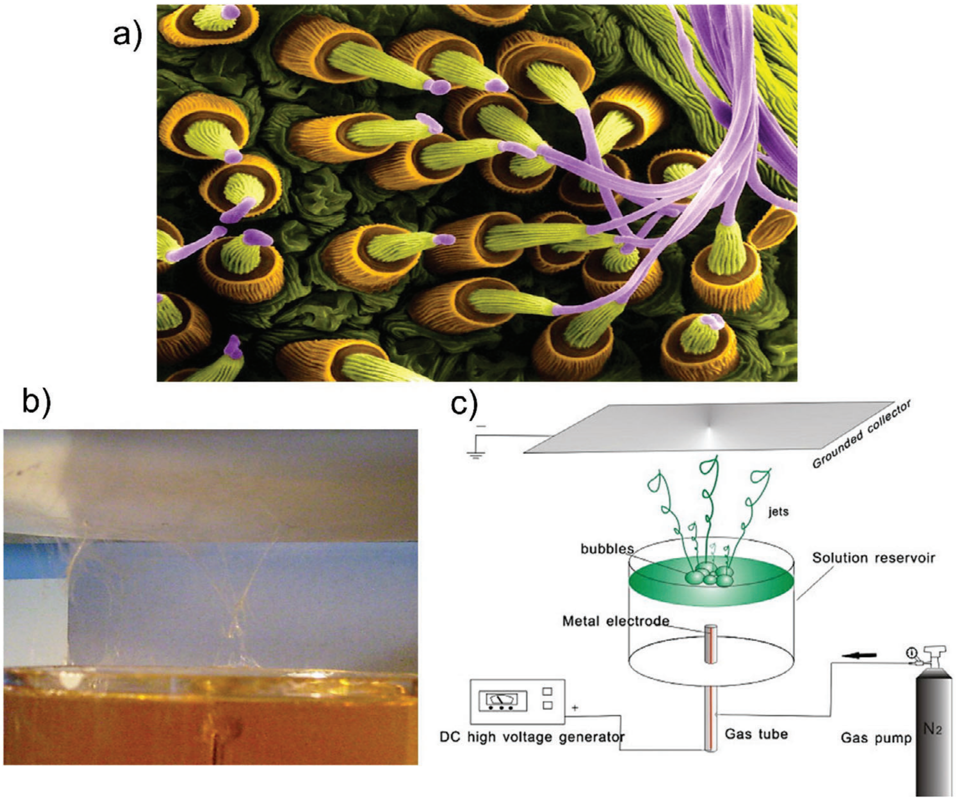

Figure 5. Schematic illustration of bubble electrospinning. a) Spider-spinning process. The diameter of a single nanofiber is ≈20 nm. b) Ejected nanofilaments captured by a digital camera. c) Schematic illustration of a bubble electrospinning system. Reproduced (Adapted) with permission.[111] Copyright 2008, Elsevier.

surface tension is its independence from the properties of the electrospun solutions.

3.8. Near-Field Electrospinning Technique

In 2006, a groundbreaking technology called near-field electrospinning (NFES) was introduced by Sun et al. (2006),[113] offering precise control over the deposition of a charged, fine jet at low voltages. This innovative approach enables the deposition of nanofibers directly onto a collector with exceptional precision, preventing the jet from entering a chaotic motion stage by reducing the distance between the spinneret and the collector. NFES employs a solid probe as the spinneret, enhancing the electric field's strength and providing robust constraints to stabilize the charged jet. By manipulating the collector's motion trajectory, a straight jet can be employed to direct the creation of pre-designed patterns. This process can be conducted under microscopic observation, further enhancing the precision of nanofiber customizability. The visual operation not only enhances the versatility of electrospinning but also paves the way for integrating electrohydrodynamic printing technology into micro/nanosystem fabrication.[113]

Conventional electrospinning involves the application of an electric field to elongate a fine jet emerging from a Taylor cone. As the charged jet embarks on a brief stable trajectory, it soon succumbs to chaotic motion due to the Coulomb repulsive force. Consequently, nanofibers are randomly deposited on the collector, forming a nonwoven nanofibrous membrane.[114,115] The straight, stable jet is instrumental for achieving controlled nanofiber deposition. However, due to uneven electrical field strength and the impact of Coulomb repulsion, the length of the straight, non-spiraling jet is limited to a mere 0.5–3 mm.[116] The stretching and thinning of the jet occur during the chaotic motion stage, playing a pivotal role in reducing jet and nanofiber diameters.[116] The initial stable stage of the charged jet exhibits a modest stretching ratio, posing challenges in producing ultrafine nanofibers over the short distance between the spinneret and the collector. Sun et al.[113] introduced the concept and mechanism of NFES to address these limitations.

4. Slow Release of Mosquito Repellents through Electrospun Nanofibers

Controlled release is an important technology used to retain the supply of a reagent and to permit the release of the active ingredient to the target at a controlled rate, in an ideal case, keeping its amount in the electrospun nanofibers system within the optimal limits for an extended period.[36–38,117,118] Controlled-release technology has advantages such as i) prolonging the activity by providing a continuously low quantity of insect repellent at a level enough to perform its role for an extended time, ii) reducing environmental contamination, and iii) cost reduction by eliminating the time and cost of repeated and over-applications.[38,119–123]

Therefore, this reduces the unwanted lateral effects of composite losses, including mosquito repellent loss by evaporation and degradation or the masking of any odors, since toxic material becomes chemically nontoxic when combined with polymers.

To give long-lasting safety, trapping mosquito repellents in textile materials has been considered as an attractive alternative, effective and innovative method.[30–32] The microencapsulation method has enabled the enhancement of the durability of the ideal influence in multipurpose textile finishing.[33,34] Polymer coating technology was employed earlier to obtain desirable textile properties.[30]

Mosquito repellents are essential, as the other methods of protecting people against mosquito-borne malaria are not as effective.[35] A mosquito-repellent electrospun polymeric nanofiber is one of the innovative approaches that has been developed recently. These devices are used to improve the performance or prolong the activity/efficacy of a drug (i.e., repellent) via polymeric encapsulation and regulating the release rate of the drug.[10,12] For example, the slow-release mosquito repellents guarantee a constant release of active ingredients and maintain the maximum period of effectiveness of the mosquito repellents, prolonging their protection against mosquito bites.

The literature shows that various studies have reported on the use of electrospun polymeric nanofiber to attain varying drug release rate profiles, such as a rapid or immediate release, sustained release, prolonged release, delayed-release, on-demand release, as well for release with multiple phases, and the co-delivery of multiple components based on the disease obligation.[10,12]

To select the best slow-release system that releases the optimum quantity of insect repellent with minimum biological or ecological secondary risks effects as the following factors need to be considered: i) Polymer nature (thermal characteristics, crosslinking level, compatibility with insect repellent); ii) The stability of the polymer incorporated with the insect repellent during melt processing; iii) the desired release rate; iv) the shape and size of the final product; v) protection time; vi) seasonal conditions, and vii) cost and ease of formulation and application.[1,37,124]

Studies focused on the manufacture of insect-repellent-based textile formulations have recently increased. According to Chatha et al.,[30] an insect repellent applied to textile formulations retains its effectiveness for a longer time compared to one applied directly on the human skin. For example, cotton and nylon fabrics are typically treated with insect-repellent drugs, as they are widely applied in home textiles and mosquito nets. Protection-based insecticide textiles are divided into insecticidal nets, curtains, home textiles, and military uniforms and applied as a shielding barrier against adult mosquitoes and other insect bites.[30,39,45,125–129] It has been demonstrated that the insect repellent-based textile strategy was more effective in protecting people against mosquito bites.[30,39,53] The chemistry and description of several insect repellent-based textile finishes are summarized in detail and is shown in **Table 2**.

From Table 2, bioassay results have revealed that treated fabrics can be stored at room temperature for 18 months keeping their efficacy. Additionally, in terms of wash durability of devices-based repellents, it has been shown that washing repellent-treated fabrics does not substantially reduce their effectiveness. Ardanuy et al.[48] also demonstrated after 50 washing cycles the fabric could retain about 11% of the initial amount of permethrin; nonetheless, it was enough to provide a 100% knockdown of mosquitoes in 120 min and total mortality after 24 h of exposition. For example, the high quantity of repellents remaining after washing the Monochlorotriazinyl-β-cyclodextrin (MCT-β-CD)-finished cotton fabrics may be due to trapping of insecticides of insecticides into the cavities of cyclodextrins (CDs). This may be due to the cyclodextrin and insecticide binding to each other to form an inclusion complex, wherein the insecticide acts as a gent molecule nesting in the center of the hydrophobic interior of the cyclodextrin. The inclusion complex binds to fabric and allows the insecticide to remain attached to the fabric, even after repeated washing, thereby prolonging the insecticidal effectiveness of the fabric.[44]

This review demonstrated that wash durable mosquito repellents treated fabrics wherein the active ingredient is easily incorporated into the fabric can be washed, thereby maintaining the mosquito repellents at the fabric surface to permit interaction with target arthropods for a prolonged period. Thanks to the high laundering durability, strong anti-mosquito effect, and ease of application, the repellents such as permethrin-containing sol–gel coatings, could be proposed as an alternative to well-established treatments for cotton textiles, such as formaldehyde-urea resins or other polymer-based processes and electrospinning technique can be a great technique to produce these devices.

4.1. Mechanism of Insect Repellents Release through Electrospun Nanofibers

The release rate kinetics of the drug (insect repellent) can be accomplished by applying various insect-repellent slow-release strategies during electrospinning or post-electrospinning. In addition to knowing the release rate kinetics of insect repellent, the release mechanism via polymeric nanofiber should also be studied.

Several studies on the mechanism of the release drugs through polymeric nanofibers have been done.[10] Overall, the mechanism of release of a drug is a complex process and a function of various parameters that also influence the release rate of the drug (i.e., insect repellent).[10,11] These factors include i) physico-chemical properties of the drug such as solubility, stability, molecular size, and charges, as well as and chemical interaction of the insect repellent with the polymer matrix; ii) structural properties of the polymeric matrix which includes morphology, specific surface area, porosity, size, fiber entanglements, and orientation, therefore, these govern the insect repellent diffusion into the release media; iii) the release environment, and iv) probably the interactions of all these factors.

Besides the factors outlined above, the physiological parameters which include temperature, pH, temperature, and ionic strength also significantly affect the drug kinetic release profile.[10,11] In the next section, the factors that affect the insect repellent delivery from electrospun nanofibers will be comprehensively reviewed.

For the development of a polymeric-based drug (i.e., insect repellent) delivery system, it is important to comprehend the relationships between all of the above-mentioned factors. For example, the release of insect repellent from polymeric nanofibers is conducted through a diffusion process, typically governed by

Table 2. Summary in details of the type of textile finishing, chemistry, and description of several repellent-based textile finishes.

Type of textile finishing	Chemistry	Descriptions	Effectiveness and wash durability	Reference
Longer-lasting mosquito repellent finishing	Pyrethrum, pyrethrins, permethrin was applied.	Development of mosquito repellent clothing, tents, and netting for mosquito bites control.	Curtain fabric made of cotton/linen shows the highest mosquitoes repellent retention capacity and highest resistance against washing compared with 100% cotton or cotton/viscose or polyester-based curtain fabrics.	[40]
Durable mosquito repellent finishing	Cotton fabrics treated with a system with cypermethrin, a polymer, and cross-linker, by Polymer-coating & surface coating method.	Nets or curtains for personal protection indoors were used to reduce malaria morbidity and overall child mortality.	Treated-fabrics obtained, either by impregnation method or by surface-coating method, can be stored at room temperature for 18 months without loosing their efficacy. Washing cypermethrin-treated fabrics does not substantially reduce the insecticidal effect after washing.	[41]
Finishing to develop long-lasting toxic activity against mosquitoes	Treatment of cotton fabric containing bioallethrin either by trapping method or surface coating method.	Treated fabrics found applications in home textiles and curtains due to its high efficacy, uniformity, low cost, and non-toxicity.	The treated fabric can be washed and stored while keeping their insecticidal property. The high mortality of mosquitoes and excellent repellency make the coating as well as the impregnation methods of treatment a good means for the treatment of netting material provided that bioallethrin insecticide is the candidate.	[42]
Durable insect repellent textile finishing	Cotton fabrics based- limonene formulations were treated by usual coating method.	Finished fabric imparts toxic activity against mosquitoes	Bioassay test results expressed as repellency, knockdown and mortality were taken as a measure of toxic activity. The treated fabric can be washed and stored while keeping their performance.	[43]
Repellent textile finishing	Cotton fabrics with cypermethrin and prallethrin along with cyclodextrin.	The cotton fabrics-based repellents showed rapid repellent activity, slower knockdown performance, and killing activity.	The bioassay results show that for monochlorotriazinyl-β-cyclodextrin (MCT-β-CD)-finished cotton fabrics treated with cypermethrin, the retention percent after washing of the repellent action is 82%, and for knockdown 72%, and 65% for mortality	[44]
Mosquito repellent finishing	Textile finishing contained pyrethroid insecticide; bifenthrin	The product textile was applied in long-lasting insect repellent-treated mosquito nets.	The high mortality of susceptible mosquitoes and excellent blood feeding inhibition of susceptible and resistant strains made bifenthrin a good candidate for treatment of netting materials.	[46]
Mosquito repellent finishing	Mosquito-repellent finishes for textiles using essential oils derived from herbal extracts.	Safety in tropical countries. Protection of people against diseases such as malaria, and dengue fever transmitted by mosquitoes.	The essential oils-based textiles repelled mosquitoes even after 3 washes.	[47]
Textile finishing containing Permethrin systems	Permethrin was trapped into the cotton fabrics through a silicon oxide Nano-coating used via typical padding followed by curing.	Directly applied in in clothing, netting, camping gear, and military uniforms.	Nano-coated textiles showed a good insecticide effect after 50 washing cycles.	[48]
Repellent finishing treated with botanical extracts.	Crude leaf extracts of *E. alba* and *A. paniculata* with five different solvents benzene, hexane, ethyl acetate, methanol, and chloroform.	Used in different textiles with low cost and environment-friendly nature to control insects.	It was concluded botanical extracts-based textiles was an excellent potential for controlling An. stephensi mosquitoes.	[49]
Mosquito repellent finishing	Finishes based on Nanoparticles of *Vitex negundo* (essential oils)	Treated fabrics maintained their performance even after 15 washes. Because of its durability, found various applications.	The treated fabrics showed 100% mosquito-repellent efficiency. The nanoparticles loaded with *V. negundo* leaf extract-treated fabrics retained their activity until 15 washes.	[50]
Mosquito repellent finishing	Polyester textiles microcapsule of lemongrass oil for mosquito repellent finishes	Durable and reusable textiles for various medical applications	The results show that, the microencapsulated polyester fabric showed the highest mosquito repellent activity (92%).	[51]
Mosquito-repellent finishing of cotton textiles	Finishes are applied to textile material using Microencapsulated citronella oil, by the pad-dry method.	Cotton fabrics for home textiles, bed sheets, curtains	Fabrics treated with microencapsulated citronella presented a higher and longer-lasting protection from insects assuring a repellent effect higher than 90% for three weeks.	[52]

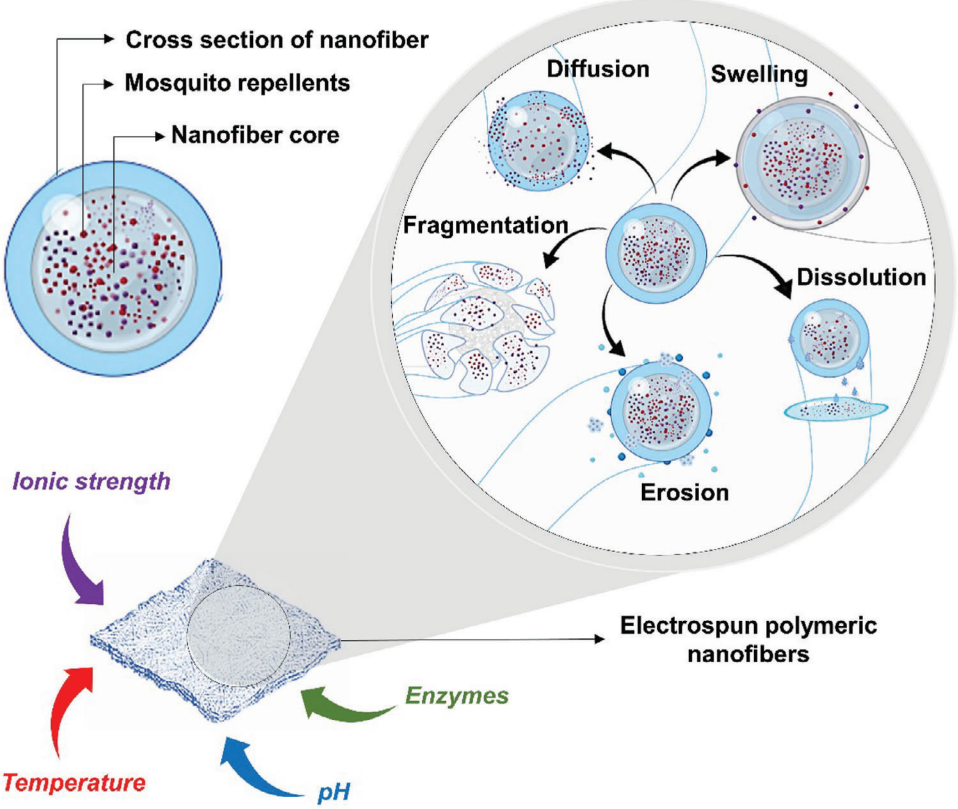

Figure 6. Schematic illustration of the drug (repellent) release mechanism from electrospun polymeric nanofibers. Reproduced (Adapted) with permission.[10] Copyright 2023, RSC.

Fick's law for biodegradable polymeric materials and a non-adherence to Fick's law for non-degradable polymer materials or complex polymeric matrices.[10,13] Mapossa et al.[54] reported and discussed several strategies used for controlling the release mechanism of insect repellents in various controlled-release systems including polymer microcapsules, nanoemulsions, solid lipid nanoparticles, polymer micelles, and liposomes microporous polymers as carriers of repellents.[1] It was noted that depending on the type of formulation, the mechanism of release of the active ingredient (insect repellent) can be controlled by diffusion, degradation, and swelling followed by diffusion. In the case of polymeric nanofibers, firstly, when the nanofibrous mat is kept in the release media, the surface-active ingredients diffuse into it. Ultimately, the release media occupies the interfibrous pores, and the polymer matrix swells. Due to swelling, the release media becomes more accessible to the inner drug molecules (insect repellent), and additional diffusion takes place. Therefore, during the first stage, the diffusion is in harmony with Fick's second law. Next, due to the fused nanofibers, slow diffusion occurs. In the third step, polymer materials degradation commences due to enzymatic hydrolysis. The degradation process occurs at the surface and within the bulk polymer, with additional support in the diffusion of the outstanding surface and bulk molecules. **Figure 6** shows a schematic of the drug (repellent) release mechanism.[10] Therefore, for controlled release of the insect repellent, an understanding of the fundamentals behind drug diffusion through polymeric nanofibers is needed. Overall, the diffusion of drugs, the swelling of polymer devices, and the degradation of material are considered the principal mechanisms involved in the repellent release through polymeric nanofibers.[1,10] Finally, it is important to note that all three mechanisms do not necessarily occur simultaneously.[10]

The morphological properties of electrospun polymeric nanofibers containing insect repellents have been evaluated by microscopy methods. For example, the morphological features of PLLA fibers with different amounts of DEET are shown in the SEM micrographs in **Figure 7**.[16] For all investigated concentrations, the polymeric nanofibers show a smooth surface and display a uniform and regular bead-free structure. With a high concentration of insect-repellent DEET, the cross-section switches from circular to flat-ribbon-like morphology.[16] The authors also reported that the pure PLLA fibers demonstrated a diameter distribution known as a bimodal fiber comprising two families of nanofibers and microfibers presenting sizes of diameters less than 0.5 and close to 2 μm (Figure 7a). For PLLA fibers impregnated with insect-repellent DEET, a monomodal distribution was obtained as shown in Figure 7b–e. Additionally, the study showed that the diameter distribution of electrospun polymeric nanofibers becomes narrower with the increase in the concentration of DEET. In general, this study demonstrated that the incorporation of insect repellent into the PLLA fibers presented a slight influence on the average fiber diameter of PLLA, and also on the diameter distribution. The average diameter of DEET-based PLLA fibers is ≈1.5 μm.[16]

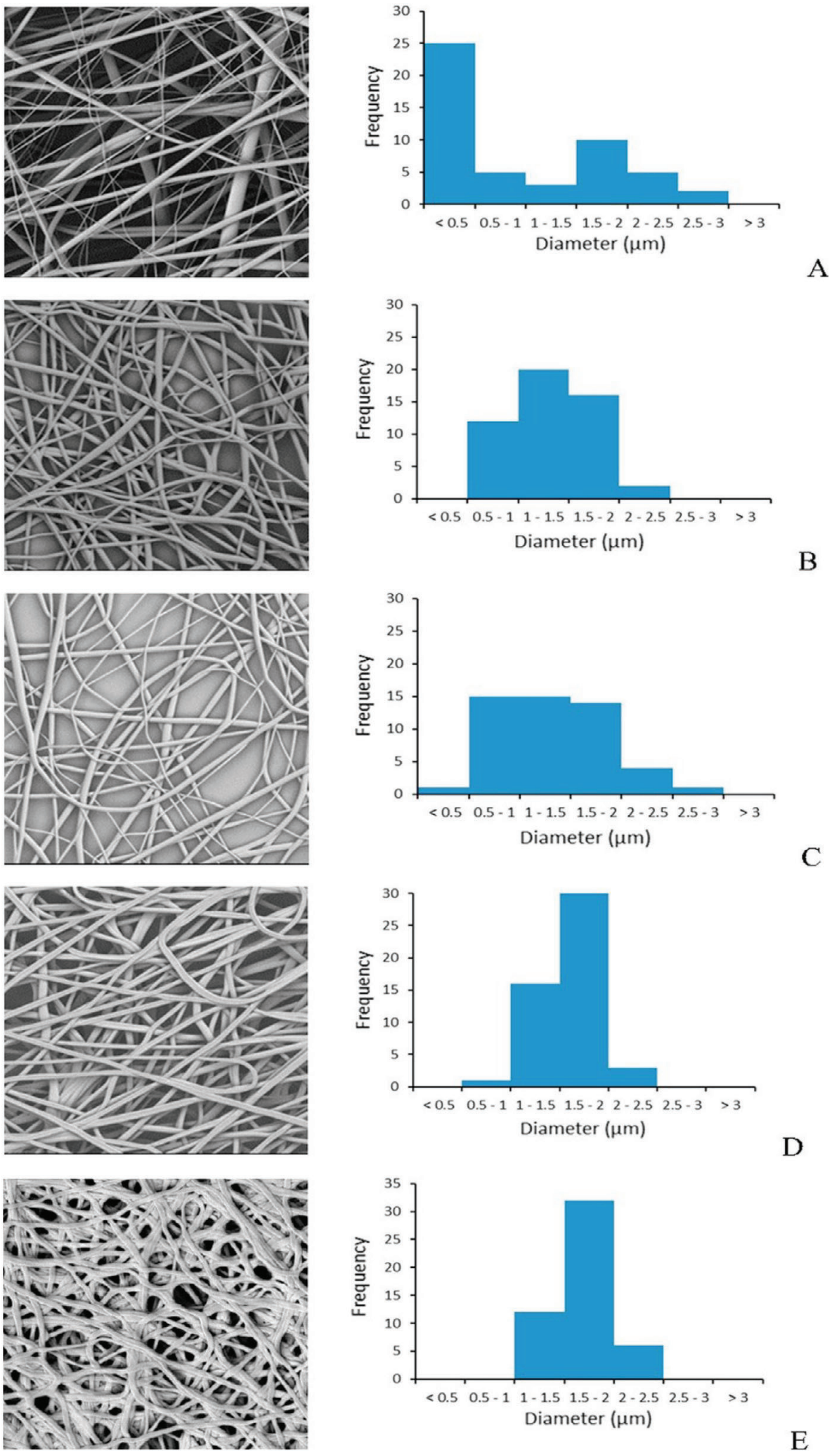

Figure 7. SEM micrographs and diameter-distribution of fibers of PLLA/DEET/$CHCl_3$ formulations with varying amounts of DEET: a) Neat PLLA (P15D0); b) 100 μL of DEET (P15D1); c) 200 μL of DEET (P15D2); d) 300 μL of DEET (P15D3); e) 400 μL of DEET (P15D4). Reproduced (Adapted) with permission.[16] Copyright 2019, Elsevier.

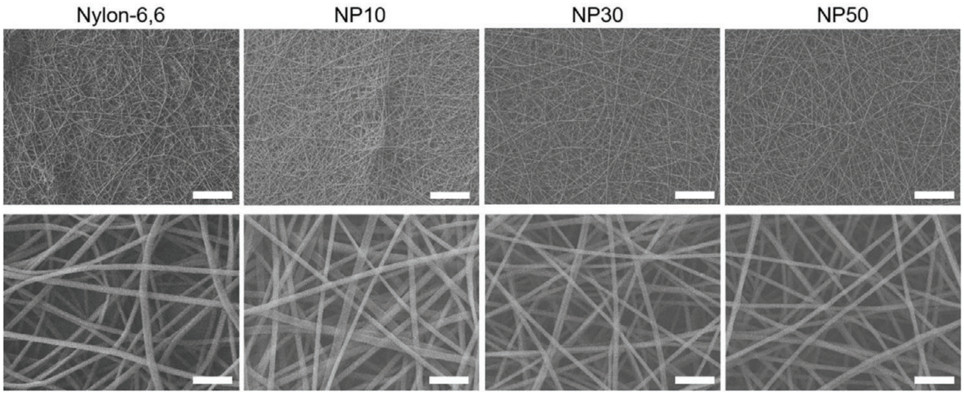

Figure 8. SEM micrographs of electrospun Nylon-6, 6 nanofibers containing picaridin. The scale bars are 20 µm (top) and 2 µm (bottom). Reproduced (Apdated) with permission.[14] Copyright 2020, Wiley.

In another study, Ryan et al.[14] showed that the morphology and size of nanofibers were largely unaffected by the incorporation of picaridin at very high loading (i.e., 50 wt%) as is presented in **Figure 8**. The results were attributed to the picaridin loading having a slight influence on the initial electrospinning polymer solution viscosity and dielectric properties, in spite of the noteworthy weight contribution of picaridin to polymeric nanofibers after electrospinning. As the amount of picaridin did not have negative effects on morphology and size, potential development and use of such fibers for repellent textiles are not limited by picaridin loading levels.[14]

However, Bonadies et al.[20] previously demonstrated that higher concentrations of insect repellent, i.e., more than 50 wt.% DEET resulted in fibers with more defects due to unfavorable microstructure development and phase behavior. This is undesirable in the development of durable fabrics and textiles.

To obtain information regarding the structural properties of the polymer, the structure of the insect repellent trapped into the polymer fibers, and to evaluate the level of interaction between the active ingredient and the polymer matrix, the Confocal Raman spectroscopic method can be employed.[22,23] This method is thus used to confirm the presence of insect repellent incorporated into polymeric nanofibers. Ciera et al.[22] optimized the electrospinning technique in fabricating PVA nanofibers with various concentrations of insect repellents permethrin, PMD, chilli, and catnip oil repellents in PVA nanofabrics. The Raman spectra of the PVA nanofibers containing insect repellent confirmed peaks for both PVA and their respective insect repellents, showing that all the insect repellents were trapped in the PVA nanofibrous formulations (**Figure 9**).

Studies on mosquito control have shown that insect repellent-based electrospun polymeric nanofibers offer a potential alternative to extend the period of protection against mosquito bites while avoiding contact between mosquitoes and the human skin. For example, in the study conducted by Sibanda et al.,[24] they employed melt spinning to fabricate bicomponent fibers with poly(ethylene-co-vinyl acetate) containing DEET as the core surrounded by a high-density polyethylene (HDPE) sheath. They fabricated socks using these bicomponent fibers which have long-term effectiveness against mosquito bites for 33 weeks even after 20 cold washes of the socks. Ever since the study by Sibanda et al.,[24] there have been further developments in this field.[24] For example, recently electrospinning was used to fabricate recycled poly(ethylene terephthalate) microfibers containing the insect-repellent DEET.[15] Thermogravimetric analysis (TGA) demonstrated that the fibers delayed the release of the insect repellents (DEET and picaridin) and they were effective against bites from the mosquitoes *Aedes aegypti*. 100% of protection was observed for 1 week and 80% was achieved for 3 weeks. Iliou et al.[130] also showed that the insect-repellent citronella oil-based biodegradable polymers cellulose acetate and polyvinylpyrrolidone micro/nanofiber displayed extended release of citronella oil and a high repellent activity in laboratory bioassays against the mosquito *Aedes albopictus* for at least 4 weeks. These studies suggest that it is possible to trap a high amount of insect repellent in electrospun polymeric nanofibers, sufficient to control insects for a long period of time. The studies also suggest that the nanofibers have the capacity to decrease the high volatility and degradation of insect repellents, they also improve the stability of the insect repellents, and they keep the minimum effective amount required and enable their effective application.

5. Factors Affecting the Release Rate of Repellents from Nanofibers

Nanotechnology has significantly advanced, particularly in developing nanofibers impregnated with insect repellent substances. The innovation signals a revolutionary approach to combating insects, especially mosquitoes, which are responsible for the transmission of diseases of great epidemiological relevance, such as dengue, Zika, and Chikungunya.[1,27] The distinction of nanofibers does not lie merely in the incorporation of insect repellents but, more precisely, in the controlled release methodology of the substances. In contrast to conventional insect repellents, whose topical application is susceptible to removal or dilution, nanofibers guarantee a modulated and consistent release of the insect repellent compound, enhancing efficiency and longevity.

However, achieving optimal release is an intricate issue. Effective system performance is not determined solely by the presence of the repellent but by a multifactorial interaction that influences release. The factors can be classified into two categories: intrinsic,

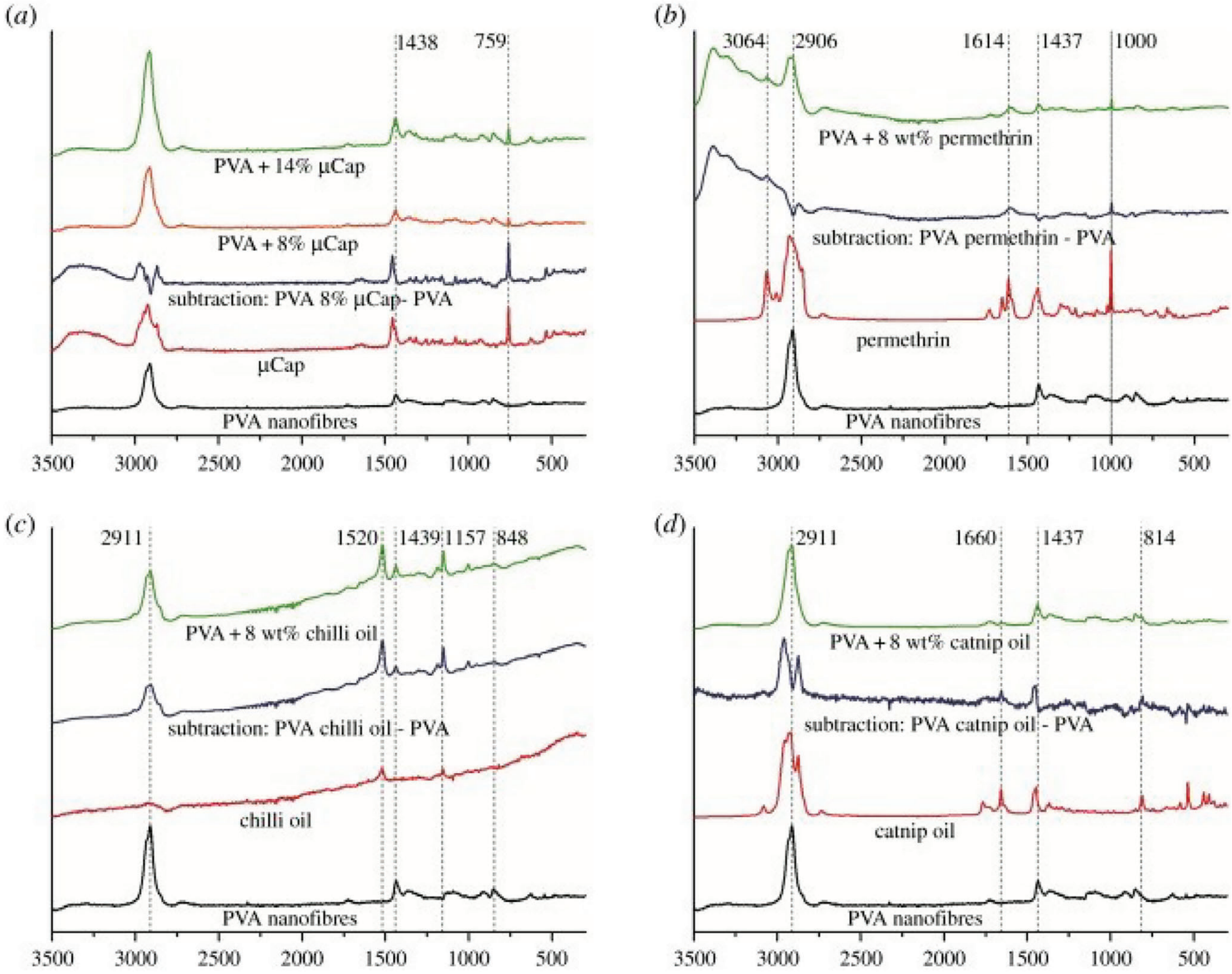

Figure 9. Raman spectra of PVA nanofiberswith PMD micro-capsules (a), permethrin (b), chilli oil (c), and catnip oil Reproduced (Adapted) with permission.[22] Copyright 2019, RSC.

associated with the composition and structure of the nanofiber and the repellent, and extrinsic, related to environmental conditions, such as variations in temperature, humidity, and interactions with other substances.[119] A thorough understanding of the interactions between factors is of paramount importance for the development of more refined solutions. For example, the careful selection of the polymer used in the nanofiber, the specific concentration of the repellent, and the morphology and porosity of the fiber are crucial elements that determine the rate and pattern of insect repellent release.[120] At the same time, environmental factors, such as relative humidity and temperature, can modulate this release. In this sense, nanotechnology, proposed to establish more robust defenses against insect vectors, is positioned as a promising solution for preventing diseases transmitted by mosquitoes. However, to fully capitalize on the potential, an in-depth understanding of the multiple factors that govern the release of repellents is imperative. Thus, through knowledge of the variables, the effectiveness of materials can be improved and maximized.

5.1. Intrinsic Factors

The evolution of nanotechnology, combined with the emerging need to develop practical solutions to combat disease-carrying insects, has culminated in the production of nanofibers impregnated with insect repellents. Nanofibers distinguish themselves not only by their ability to contain insect repellent agents but also by their method of releasing these agents into the environment, which ultimately dictates their effectiveness and duration. A series of intrinsic factors related to the composition and structure of the nanofibers and insect repellents play a fundamental role in this release process. Intrinsic factors cover a wide range of characteristics, from the chemical nature of the polymer used to make the nanofiber, the morphology, and porosity of the fiber, to the concentration and type of insect repellent incorporated.[121] The interaction between factors, as well as individuality, can significantly influence the insect repellent release kinetics, diffusion profile, and long-term protection capacity. In the following section of the review, the main intrinsic factors that influence the release of insect repellents from the nanofibers were explored in detail, highlighting their relevance and potential implications for optimizing functional textiles intended for protection against insect vectors.

5.1.1. Nanofiber Composition

Within the scope of strategies to combat insect disease vectors, nanofiber composition emerges as a central element, especially concerning the impregnation and subsequent controlled release of repellents. Nanofibers are often made of polymers. Polymers can be of natural origin, for example, cellulose and chitosan, or synthetic, as is the case with polyester and polyethylene.[122–124]

The composition is intrinsically linked to the physical, chemical, and mechanical characteristics of the final material.[125] These characteristics directly affect the nanofiber's ability to interact with the insect repellents, as well as the efficiency of release over time. For example, polymers with greater absorption capacity can retain the insect repellent more effectively, ensuring a gradual and continuous release. Kadam and co-workers adopted an interfacial polycondensation methodology for encapsulating DEET.[119] The process was carried out using modified cellulose nanofibers that perform the function of pickering emulsifiers. The research findings indicate that nanofibrillated cellulose, when functionalized with stearic acid, promotes the formation of stable two-phase emulsions (oil–oil and water–oil). Furthermore, functionalized nanofibers have been shown to be exceptionally efficient at encapsulating DEET, achieving an efficiency rate of approximately 98%. Also, the functionalization of the nanofibers not only served as a pickering emulsifying agent but also significantly improved the barrier characteristics of the microcapsules, culminating in a substantial reduction in the DEET release rate, which suggests a potential improvement in the material's performance in practical applications.

It is equally relevant to consider the molecular interactions between the polymers and the insect repellents. Depending on the chemical nature of the polymers and the insect repellents, stable bonds can be formed in-between them. Polymers that establish more robust interactions with certain insect repellents can serve as long-lasting reservoirs, releasing the insect repellent in a prolonged manner.[126] In contrast, polymers with a lower affinity or more open structures may facilitate a faster and less controlled insect-repellent release. In the context of research into innovative textile materials, Fulton and coworkers conducted a study pertinent to the synthesis and evaluation of recycled polyethylene terephthalate microfibers, which were impregnated with the insect repellents DEET and picaridin through an electrospinning process.[127] The microfibers produced demonstrated substantial retention of the insect repellents, with an efficiency of up to 97% after processing.

In the study by Fulton et al. (2023), with respect to the insect repellent effectiveness, it was observed that the fibers maintained complete protection (100%) for more than a week and considerable effectiveness (80%) for a period extending beyond three weeks.[127] The findings signal significant potential for large-scale application in the textile sector, offering long-lasting insect repellency. Therefore, the composition of the nanofiber plays an essential role in determining the effectiveness and durability of protection against insect vectors, which, depending on the nanofiber, directly impacts the release profile of the compound.

5.1.2. Fiber Dimensions and Structure

The composition of the nanofiber is intrinsically linked to morphology, which encompasses characteristics such as shape, surface, and internal structure. The morphology directly influences the nanofiber's ability to impregnate and release insect repellents, two crucial factors for its effectiveness in combating insect vectors. When analyzing the dimensions and structure of the fibers, the morphology of the materials can vary considerably depending on the composition. Nanofibers that have rougher or more porous surfaces, for example, tend to have an increased capacity for incorporating insect repellents. Surface irregularities act as small reservoirs, enabling the storage of a greater quantity of insect repellent and, consequently, the controlled release of the substance.[128]

Furthermore, the internal structure of the nanofiber also plays a preponderant role in the process. Fibers with a denser configuration can release the insect repellent gradually since the substance must travel through a more compact matrix to reach the surface. On the other hand, fibers with a more open internal structure can provide a more accelerated release of the insect repellent, although the action may be short-lived.[129]

Iliou and co-workers studied the use of functional nanofibrous matrices in developing sustained-release systems for insect repellents.[130] The focus of the study was on the applicability of matrices as controlled distribution mechanisms for insect-repellent substances, with an experiment that consisted of electrospinning matrices comprising cellulose acetate and polyvinylpyrrolidone, which were enriched with citronella oil. Both single-layer and multi-layer nanofiber structures were examined to discern the impact of surface layers on insect repellent release efficiency.

The results indicated that all nanofiber configurations tested maintained a continuous release of the insect repellent for a minimum of four weeks. However, it was observed that matrices with citronella oil incorporated into cellulose acetate, both in single and triple-layer configurations and in the PVP-CA-PVP triple-layer system, presented a slower and more consistent release profile, maintaining a more significant amount of insect repellent after the end of the evaluated period. The finding suggests significant potential for using these nanofibrous matrices in practical applications, offering an effective and long-lasting solution for protection against insects.

It is also imperative to highlight the importance of the shape of the nanofiber. Depending on the manufacturing methods and composition, nanofibers can be cylindrical, spiral, and branched. Each configuration offers a specific surface area, thus influencing the ability to retain and release the insect repellent. Ryan and coworkers used electrospinning to create functional fibers with hierarchical micro- and nano-level structures, targeting a tunable release of insect repellent.[131] They were successful in physically incorporating picaridin into nylon-6, 6 nanofibers without changing the size and morphology of the fibers, even at high incorporation levels of up to 50 wt%. The release of picaridin from the fibers was shown to depend on both the concentration of the substance and the environmental temperature due to the minimal intermolecular interactions between picaridin and nylon, which allowed a predominantly diffusive release.

Furthermore, in the study by Ryan et al.,[131] the team innovated by developing coaxial nanofibers, in which the outer layer protects the additives in the core, giving the material more excellent durability and acting as an additional barrier to diffusion to prolong the release of the insect repellent. These coaxial fibers presented a different release profile than conventional monofilament fibers, demonstrating the method's effectiveness in modulating the insect-repellent release behavior. Thus, the morphology of the nanofibers, strongly influenced by the composition, is decisive for the performance efficiency.[2] An in-depth understanding of the morphological characteristics of the nanofibers has been essential in continuously improving their functionality and, consequently, their effectiveness preventing insect-borne diseases.

5.1.3. Insect Repellent Concentration

The appropriate concentration of insect repellents impregnated into nanofibers is an essential variable. The amount of the insect repellent present in nanofibers not only determines the effectiveness of protection but also affects other relevant properties, such as the durability of the insect repellent action and the physical and mechanical characteristics of the fiber. It is essential to understand that the ideal concentration of the insect repellent in a nanofiber is not a universal constant. Variables such as the type of insect repellent used, the composition of the nanofiber, the impregnation method, and the purpose of application play crucial roles in determining this concentration.[2,126] Furthermore, it is necessary to balance the amount of repellent to ensure adequate protection without compromising the integrity or functionality of the nanofiber. An excessively high concentration of repellent can, in some cases, lead to saturation of the nanofiber, causing too rapid release of the repellent and, consequently, short-term protection. On the other hand, a low concentration may not be sufficient to offer adequate protection against the target vectors.

Muñoz and coworkers developed ethylcellulose nanofibers with insect-repellent activity, incorporating citriodiol, a biological insect repellent derived from natural and renewable sources.[2] The study focused on the influence of the characteristics of the electrospun solution, such as viscosity and surface tension, on the formation and morphology of the resulting fibers, in which they identified that the mixture of Ethanol/N, N-dimethylacetamide (30/70) was the ideal system for manufacturing nanofibers impregnated with the insect repellent. The research revealed that the formation of uniform, defect-free nanofibers was possible when the citriodiol content was kept below 50%. However, when the concentration of the repellent was increased, the formation of fusiform structures and agglomerates was observed, resulting in "lagoons" in the fibers, indicating a change in the morphology and rate of release of the substance. Thus, the study not only highlighted the feasibility of using citriodiol in ethylcellulose nanofibers for insect repellency but also noted the importance of electrospinning solution properties and repellent concentration in determining the final quality of the nanofibers.

Therefore, it is essential to find a balance that maximizes the effectiveness and duration of protection without causing adversity to the material or the user. In addition to the effectiveness of repelling insects, insect repellent concentration can also influence properties such as flexibility, and permeability of the nanofiber. In some cases, the insect repellent can act as a plasticizer, increasing the material's flexibility.[1,131,132] In others, it can make the fiber more rigid or brittle. Therefore, determining the appropriate concentration of repellents in nanofibers is a complex task that requires a deep understanding of the interactions between the repellent and the fiber material, as well as the specific objectives of the application in question. Continuous research in this field is essential to optimize the insect repellent concentration and thus maximize the effectiveness and functionality of nanofibers impregnated with insect repellents.

5.1.4. Nature of Insect Repellent

The chemical nature of the insect repellent incorporated into the nanofibers is of fundamental importance in determining the efficiency and functionality of advanced materials. The specificity of the insect repellent, in terms of composition and physicochemical properties, not only regulates its intrinsic ability to repel insects but also establishes technical criteria related to the stability, durability, and release modality of the said compound. The chemical profile of the insect repellent can be analyzed from different perspectives: solubility, volatility, molecular weight, structural configuration, and reactivity.[126] Each of the parameters has a direct impact on the interaction of the insect repellent with the polymeric matrix that constitutes the nanofiber, thus influencing the effectiveness of the protection offered. For example, insect repellents with hydrophobic characteristics tend to have high compatibility with polymers of a similar nature, resulting in homogeneous and long-lasting impregnation. On the other hand, insect repellents with a hydrophilic profile may require adaptive techniques or the presence of specific carrier agents for effective incorporation into predominantly hydrophobic polymer matrices.[132]

Konchada and coworkers reported the development of nanofibers with controlled insecticide release to repel or deter mosquitoes (*Aedes aegypti*), in which various blend compositions were prepared by manipulating the ratio of neem oil-based polyesteramide and polycaprolactone, immobilized with insecticide, transfluthrin.[133] The product-based nanofibers containing transfluthrin killed mosquitoes in 100% for 24 h. Therefore, the interaction of the insecticide with the matrix interfered with the release rate of the substance, presenting a prolonged action.

Also, the volatility of the insect-repellent compound is an aspect of relevance. High-volatility compounds tend to be released quickly, providing immediate but limited-duration protection. In contrast, low-volatility repellents promote a controlled and gradual release, ensuring extensive protection over time.[117] The structural configuration of the insect repellent can determine the ability to establish interactions, whether through hydrogen bonds or electrostatic interactions, with the nanofiber, thus modulating the release rate.[134] Finally, the chemical stability of the insect repellent is a parameter that must be addressed. Stable insect repellents, resistant to degradation by factors such as light, humidity, or oxidation, tend to present superior performance in terms of longevity when impregnated into nanofibers. In this sense, the chemical specificity of the insect repellent is a central pillar in the design and development of impregnated nanofibers. A careful analysis of the intrinsic properties of the insect repellent and the interactivity with nanofibers is essential for optimizing materials intended for protection against disease vectors, thus ensuring maximum efficiency, durability, and safety in application.

5.1.5. Integration Technique and Additive Presence

The methodology for integrating insect repellents into nanofibers is of primary importance. The chosen technique and precision in application largely determines the effectiveness and longevity of the insect repellent within the fibrous structure. The correct selection and optimization of the method guarantees a controlled and sustained release of the insect repellent, enhancing the product's effectiveness. Numerous techniques have been investigated, each with intrinsic characteristics, advantages, and limitations. Some highlighted techniques may be immersion impregnation, coaxial electrospinning, and incorporation during nanofiber formation, and post-processing methods. Immersion impregnation involves immersing the nanofibers in a solution containing the desired repellent. Subsequently, upon evaporation of the solvent, the repellent is retained on the surface of the nanofiber.[135] The method's efficiency is directly influenced by the concentration of the repellent in the solution, the immersion time, and the characteristics of the solvent used.

Coaxial electrospinning can be performed in which two solutions are simultaneously fed through a coaxial system.[121] The peripheral solution constitutes the nanofiber matrix, while the central solution, rich in insect repellent, is internally encapsulated. The method results in nanofibers with an insect-repellent core, which favors gradual release. Regarding incorporation during nanofiber formation, the insect repellent is added directly to the polymer solution before electrospinning. As a result, the insect repellent is evenly distributed throughout the entire length of the nanofiber. Post-processing techniques are characterized by additional methods, such as vapor deposition or spraying, which can be adopted to anchor the insect repellent on the surface of the fibers.

Pardini and co-workers developed an innovative microencapsulation system using the electrospray technique to encapsulate citronella oil in poly(ϵ-caprolactone) microcapsules.[136] The method aimed to create a controlled release mechanism for citronella oil, known for its high volatility and insect-repellent properties. The experiments revealed that the optimal ratio of poly(ϵ-caprolactone) to citronella oil was 3/1. Applying a voltage of 10 kV during the electrospray process resulted in microcapsules with uniform and well-defined morphology. Characterization analyses confirmed the presence of citronella oil inside the microcapsules with an encapsulation efficiency greater than 80%, attesting to the efficiency of the process. Furthermore, release tests in an aqueous environment pointed to a consistent and prolonged release of citronella oil, extending over at least forty days. Therefore, through the sustained release profile, the potential of the technology for applications in long-lasting insect repellent products is perceived, providing an effective and long-lasting solution. Thus, the integration of the insect repellent into nanofibers is a process that demands technical rigor and is linked to the performance of the material.

Parameters such as the choice of solvent, viscosity of the solution, applied electrical voltage, and temperature are paramount and must be precisely controlled to obtain an efficient product. Additionally, it is imperative to consider the chemical interaction between the insect repellent and the nanofiber constituent polymer.[137] Finally, effectively incorporating insect repellents into nanofibers requires an in-depth technical understanding of the methods and meticulous optimization of the parameters involved. Precision and rigor at this stage are critical to enhance the efficiency of nanofibers incorporated with insect repellents in combating vector agents. Each procedure for incorporating the repellent into the polymeric matrix significantly influences the mechanism and rate of release of the active compound when used.

Some in-depth studies have focused on the incorporation of additives into nanofibers containing insect repellents. Additives, which range from plasticizers to stabilizers, antioxidants, and reinforcing agents, perform vital functions that can determine the intrinsic and operational characteristics of nanofibers.[126] The presence of additives can significantly modify the morphology of the nanofiber. The modification can directly interfere with the surface, porosity, and internal structure of the fiber. Such changes can impact the storage capacity and subsequent release of the incorporated insect repellents.

Additionally, additives can improve the thermal and mechanical properties of nanofibers, ensuring that they maintain functionality under various environmental conditions. The chemical interaction between the additive and the nanofiber constituent polymer can also affect compatibility with different insect repellents. Certain additives can facilitate the homogenization of the insect repellent in the polymer matrix, increasing efficiency and durability. On the other hand, other additives can create chemical barriers that modulate the release of the insect repellent, enabling extended protection. It is imperative, however, that the selection and use of additives is carried out with rigor and discernment.

Ogilvie-Battersby and co-workers applied the complex coacervation technique to create innovative microcapsules that encapsulate geraniol using a matrix of gelatin and gum arabic.[138] The study examined how processing conditions influence the size, morphology, and release characteristics of the produced microcapsules. The optimal conditions identified for coacervation occurred at a pH of 4.45, while crosslinking was most effective at 6.0. Also, it was observed that slower agitation speed resulted in the formation of microcapsules with a larger diameter of ≈93 µm and a single nucleus. In comparison, faster agitation favored the formation of multinucleated microcapsules with average particle sizes of ≈34 µm.[138]

Interestingly, the study by Ogilvie-Battersby, et al.[138] also showed that the geraniol content in the microcapsules varied depending on the agitation rate, reaching 90%, 68%, and 73% for speeds of 700, 1000, and 1300 rpm, respectively. The microcapsules demonstrated exceptional performance in releasing the active agent consistently in high-humidity environments, without any abrupt releases. Geraniol retention rates after 26 days were substantial, remaining at 80%, 74%, and 76% for the respective stirring speeds (**Figure 10**). The study highlights the potential to

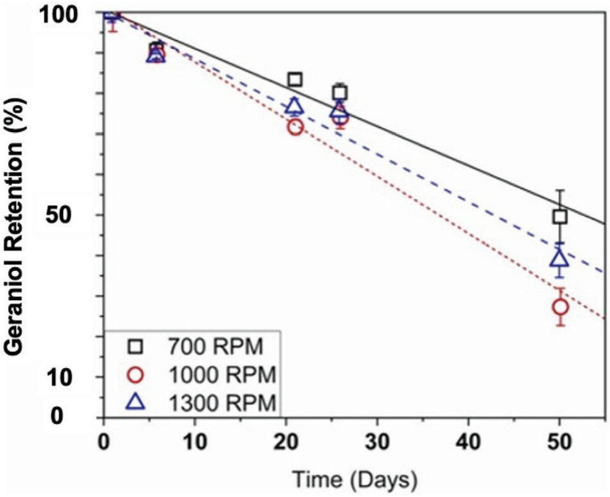

Figure 10. Release rate of geraniol from gelatin/gum arabic microcapsules. Reproduced (Adapted) with permission.[138] Copyright 2022, Elsevier.

adjust the release properties of geraniol microcapsules by manipulating processing conditions and components. This paves the way for the development of controlled delivery systems with potential applications in various fields.

Hence, detailed analysis of the interaction between additives, insect repellents, and the polymeric matrix is necessary to ensure that neither the effectiveness of the repellent nor the integrity of the nanofiber is compromised. Additionally, it is vital to ensure that the selected additives do not present toxicity or unwanted side effects when in direct contact with the dermis or the surrounding environment.[139] In summary, the incorporation of additives into nanofibers represents an innovative strategy for enhancing defense against vector agents. However, such an approach requires careful and systematic evaluation to ensure the enhancement of the desired characteristics while maintaining the safety and efficacy of the resulting compound.

5.2. Extrinsic Factors

In the context of nanotechnology, particularly in the development of nanofibers impregnated with insect repellents, it is imperative to address not only the intrinsic aspects of nanofibers but also the extrinsic factors that can affect the release rate of the insect repellents. Extrinsic factors refer to environmental variables and external conditions to which nanofibers are subjected and can directly affect effectiveness.[135] Among the environmental variables, temperature, relative humidity, and exposure to ultraviolet radiation stand out.[140] Such conditions can alter the physicochemical properties of nanofibers, significantly impacting the release of insect repellents. Additionally, mechanical factors, such as stresses applied to the fibers or friction, can also play a crucial role in modulating the release rate. The rigorous and systematic evaluation of extrinsic factors is essential to ensure that nanofibers impregnated with insect repellents perform their role optimally in various scenarios. Understanding the impact of environmental variables and external conditions on nanofibers enables adaptation and eventual modification of these materials, with the aim of tailoring them for specific environments. This ensures robust and lasting protection against disease-carrying insects. The following sections of the review focus on elucidating the extrinsic factors that impact the release of insect repellents from nanofibers, emphasizing their significance and implications in the development of specialized textile materials for protecting against vector agents.

5.2.1. Environmental Dynamics

Environmental dynamics play a crucial role in the interaction between insect repellents and nanofibers. The release rate of nanofiber insect repellents is not only influenced by the intrinsic characteristics of the fibers or the insect repellent itself but also by the environmental conditions to which the material is exposed. First, temperature is a determining factor. In warmer environments, a more accelerated release of insect repellent may occur due to the increase in the kinetic energy of the molecules.[140] This factor is particularly relevant in tropical regions, where insect vectors are more prevalent, and temperatures are, on average, higher. Also, relative air humidity is an extrinsic factor of great importance. In environments with high humidity, the ability of nanofibers to retain insect repellents may be compromised, leading to faster release. On the other hand, in low humidity conditions, the release can be more controlled and prolonged.[135]

Du and coworkers developed composite fibers by integrating poly(L-lactic acid) (PLLA) with the insect-repellent ethyl butylacetylaminopropionate (IR3535), using the solution electrospinning technique to examine the release of the insect-repellent in response to temperature variations.[140] The resulting fibers exhibited a monoaxial morphology, free from imperfections and with diameters ≈1 µm. The refined structure allowed efficient incorporation of IR3535, which could exceed 40% by mass, into PLLA fibers. Notably, IR3535 acted as a plasticizing agent for PLLA, impacting the material properties. The release profile of IR3535 from composite fibers at various temperatures, ranging from 60 to 100 °C, revealed a notable increase in the release rate of the insect repellent with rising temperature (**Figure 11**). The evaporation of IR3535 was rapid and complete in approximately 4 hours at a temperature of 100 °C. On the other hand, at a lower temperature of 60 °C, only ≈20–30% of the insect repellent was released over 12 h.

Other chemical agents in the environment, such as pollutants or volatile substances, can also interfere with the interaction between the insect repellent and the nanofiber. Depending on the nature of these agents, the substances can either accelerate or delay the release of the insect repellent. Finally, exposure to light, e.g., ultraviolet light, can degrade some insect repellents, altering their effectiveness and, consequently, the protection offered.[126,141] Therefore, when developing nanofibers impregnated with insect repellents, it is crucial to consider environmental dynamics and associated variables to ensure effective and long-lasting protection against insect vectors.

5.2.2. Surface Treatments

Surface treatments on nanofibers impregnated with insect repellents involve procedures aimed at modifying or enhancing the

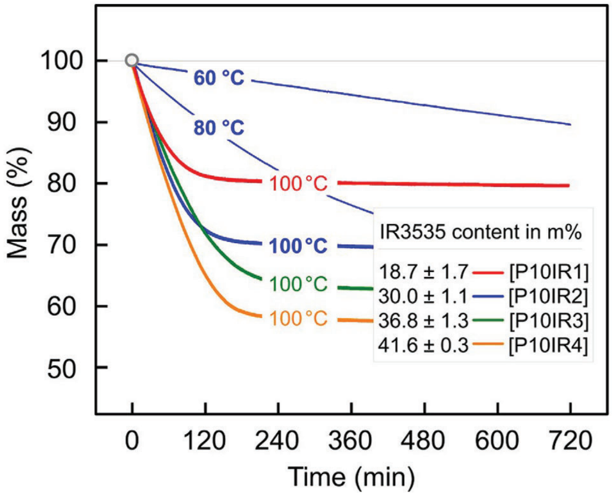

Figure 11. Release rate of ethyl butylacetylaminopropionate (IR3535) from electrospun poly(L-lactic acid) fibers. Reproduced (Adapted) with permission.[140] Copyright 2023, ACS.

surface characteristics of the fibers. The goal is to optimize the interaction with the insect repellent, thereby enhancing its effectiveness. Treatments can directly influence the insect repellent release rate, adhesion, and even resistance to degradation.[141] Chemical functionalization is one of the most common surface treatments, which involves introducing specific functional groups onto the nanofiber surface. The process can improve the affinity between the insect repellent and the nanofiber, allowing for a more controlled and uniform release of the insect repellent. Furthermore, it can provide excellent resistance to washing, which is essential for textile applications.[142,143] Also, applying coatings or protective layers on the nanofiber is a relevant treatment. The application of coatings can act as a physical barrier, delaying the release of the insect repellent and ensuring prolonged protection. Additionally, layers can offer additional properties, such as resistance to water or chemical agents.[142,143]

Plasma application is also widely used for modifying nanofiber surfaces, where the exposed material undergoes chemical and physical modifications. The treatment can increase the porosity and roughness of the surface, allowing for a more significant insect-repellent load and, therefore, more effective protection. Xiang and collaborators conducted a detailed study on the effectiveness of polyamide fabrics in repelling insects, targeting applications in mosquito protective clothing.[141] They used permethrin, applying it to polyamide fabrics during the electrospinning process, by its direct inclusion in the polymer solution, and through a subsequent immersion coating, and comparing fabrics treated with oxygen plasma and untreated fabrics. Incorporating permethrin directly into the polymeric solution before electrospinning was the most efficient method for adhering the repellent to the material.

On the other hand, treating the fabrics with oxygen plasma resulted in an increase in the amount of permethrin on the surface of the fabrics since the plasma generated carboxylic groups on the surface that increased the hydrophilicity of the fabric, favoring the absorption of the insect repellent. However, surface modification with plasma did not translate into an increase in the total amount of permethrin present in tissues compared to untreated tissues. Despite this, all fabrics treated with permethrin were effective as insect repellents, in contrast to control fabrics that did not receive treatment with the insect repellent.[128]

It is imperative to highlight that the type of surface treatment chosen must be compatible with the insect repellent in question and the final application of the nanofiber. Thus, a detailed understanding of the interactions between the insect repellent, the nanofiber, and the environment is essential to selecting the most suitable surface treatment, as surface treatments play a vital role in optimizing insect repellent-impregnated nanofibers. The techniques not only affect the rate and effectiveness of insect repellent release but also the durability and resistance of the material in different environmental conditions. Therefore, the appropriate choice and implementation of treatments are essential to maximize the protection potential offered by nanofibers.

5.2.3. Mechanical Stresses

In the development of nanofibers impregnated with insect repellents, it is vital to consider the mechanical stresses that the materials may encounter in practical applications. Stresses resulting from tension, compression, bending, and twisting can significantly impact the integrity of nanofibers.[143] Nanofibers, when used in clothing, are constantly exposed to varied mechanical forces. An applied voltage, for example, can induce stretching of the nanofiber, potentially altering the morphology, and modifying the release rate of the insect repellent. Compressions, on the other hand, can reduce the surface area of the fiber, impacting the insect-repellent release process. Wear caused by friction is also a crucial factor to be considered, which can result in the gradual removal of the insect repellent from the nanofiber surface.[128] The situation could compromise the protective capacity of the material, making frequent reapplications or replacements necessary.

Additionally, it is essential to address the interaction of mechanical stresses with other extrinsic factors. The combination of tension and humidity, for example, could lead to a more pronounced degradation of the polymer and the insect repellent.[144–146] Therefore, in-depth analysis of mechanical stresses is vital for optimizing impregnated nanofibers. Reinforcement strategies, such as the addition of components or the implementation of specialized surface treatments, can be adopted to improve the resistance of nanofibers to such stresses, ensuring effectiveness and durability in practical applications.

6. Mathematical Models for the Release Rate of Insect Repellents through Nanofibers

The advent of nanotechnology has brought about significant advancements in the field of controlled release systems, particularly in deploying insect repellents through nanofibrous matrices. These nanofibers offer a high surface-to-volume ratio, which is instrumental in facilitating the encapsulation and subsequent release of active agents in a controlled manner. The scientific challenge, however, lies in the accurate prediction and regulation of the release rates of these insect repellents, a task that necessitates a rigorous mathematical and theoretical framework.

Mathematical modeling is an indispensable tool in this endeavor, providing a formal and scientifically robust method to understand and predict the kinetics of repellent release.[144–146] The employment of these models is crucial for delineating the mass transfer mechanisms that dominate the release process from nanofibers. By incorporating variables such as the diffusion coefficient, polymer degradation rates, and the solubility of active agents, mathematical models can offer predictive insight into the release kinetics under various environmental conditions.

This study emphasizes the importance of mathematical models in elucidating the rate of repellent release from nanofibrous systems. In the following sections, the theoretical foundations and the practical applications of models such as Higuchi, Korsmeyer-Peppas, and Weibull are rigorously examined. These models offer a formalized approach to predict and customize the release profiles of insect repellents, thereby enabling the scientific community to design more efficient and effective controlled release systems. Through this exploration, it will be highlighted how mathematical models are not merely academic exercises but are crucial elements in the scientific process that guide the rational design of nanofiber-based insect repellent delivery systems.

6.1. Zero and First Order Kinetics

In the field of nanotechnology, the utilization of mathematical models to understand the release kinetics of insect repellents from nanofibrous structures is of utmost importance. These models serve as predictive tools for the rate at which the insect repellents are dispensed into the environment, providing a framework for the design and optimization of controlled release systems. The kinetic models, principally zero and first-order kinetics, are integral to understanding the release dynamics and are predicated-based on the insect-repellent concentration and its interaction with the nanofiber matrix.[146]

Zero-order kinetics are characterized by a release rate that is invariant concerning the concentration of the insect repellent within the nanofiber matrix. This constant release rate, denoted as k_0, ensures a uniform delivery of the active agent over the stipulated time frame. Mathematically, it is described by the Equation (1):[147]

$$\frac{dC}{dt} = -k_0 \tag{1}$$

where C denotes the concentration of the insect repellent, and t represents time. This model is ideal when a sustained action of the insect repellent is necessitated, as it mitigates the peaks and troughs in concentration that could lead to periods of inefficacy or excessive release.

In contrast, first-order kinetics posits that the release rate of the insect repellent is directly proportional to its remaining concentration within the nanofiber matrix. This proportionality implies that the release rate diminishes as the concentration of the insect repellent decreases (Equation 2):[147]

$$\frac{dC}{dt} = -k_1\, C \tag{2}$$

where k_1 is the first-order rate constant, this model is frequently observed in systems where diffusion mechanisms are predominant, and it is particularly relevant when the insect repellent's efficacy is concentration-dependent.

The application of these kinetic models in the development of nanofiber-based insect-repellent systems is critical for achieving targeted release profiles. Through careful selection of polymer matrices and insect repellent compounds, as well as the manipulation of nanofiber architecture, scientists can design release systems that conform to the desired kinetic order, i.e., ensures a predictable and controlled dispensation of the insect repellents, which is crucial for their efficacy in practical applications, such as mosquito control, disease prevention, and other areas where repellents play a vital role.

6.2. Higuchi Model

The Higuchi model is an integral mathematical formulation used to describe the release kinetics of active agents from porous matrices, which is particularly relevant in the pharmaceutical and material sciences fields. When applied to the domain of insect repellent release through nanofibers, the Higuchi model offers a scientific and quantitative framework to elucidate the diffusion-driven processes that govern the release rate of the insect repellent from the nanofibers.[148] Fundamentally, the Higuchi model is rooted in the laws of diffusion described by Fick's laws. The model assumes that the release of an agent from a homogenous matrix is primarily governed by diffusion and is proportional to the square root of time (Equation 3).[148]

$$Q = k_H \sqrt{t} \tag{3}$$

where Q is the cumulative amount of agent released per unit area, k_H denotes the Higuchi release constant, and t is the time variable. This square root of time dependency signifies a diffusion-controlled release mechanism, characteristic of a matrix system where the matrix dimensions remain more significant than the diffusion layer.

In utilizing the Higuchi model for insect-repellent release from nanofibers, some assumptions are typically posited. Employing the Higuchi model for insect repellent release from nanofibers enables researchers to design and predict the release profiles scientifically. This predictability is crucial for developing insect-repellent systems that offer sustained release over extended periods. It also facilitates the optimization of nanofiber fabrication parameters to customize the release characteristics to specific end-use requirements.

It is essential to acknowledge that the Higuchi model, while robust, represents an idealized system. Real-world applications may involve complex interactions between the insect repellent, the matrix, and the environment which the model might not fully represent.[149] Non-Fickian diffusion, matrix erosion, variable diffusion coefficients, and non-uniform repellent distribution are factors that may necessitate modifications to the model or complementary analytical methods to achieve accurate predictions.[150] Its application, while subject to certain limitations, remains a fundamental aspect of the design and development of advanced controlled-release formulations in the field of material sciences. **Figure 12a** represents the kinetic modeling (Higuchi) for the in vitro release of L-Carvone from a blend of poly(ϵ-caprolactone) and wheat cellulose (PCL-WC).[151]

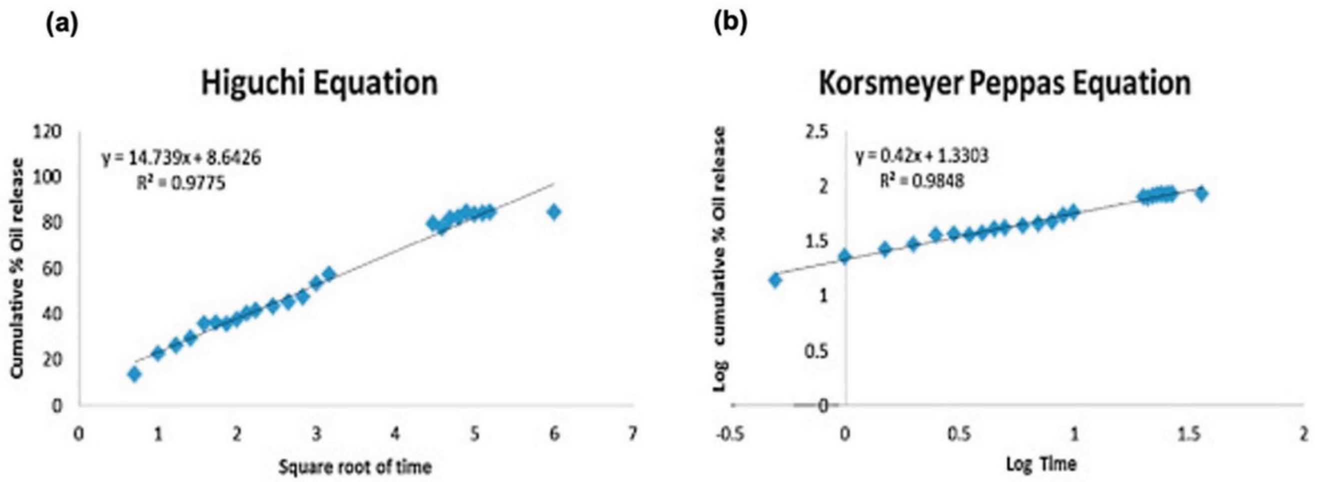

Figure 12. Kinetic modeling shows the release rate of L-Carvone from PCL-WC. a) Higuchi model; b) Korsmeyer–Peppas model. Reproduced (Adapted) with permission.[151] Copyright 2015, Elsevier.

6.3. Korsmeyer–Peppas Model

The Korsmeyer–Peppas model (Equation 4) is semi-empirical and widely used in pharmaceutical sciences to describe drug release from polymeric systems.[148] The model is particularly relevant in the study of controlled release through nanofibers. This model is applied when the release mechanism is not well-known or is controlled by more than one type of phenomenon, such as a combination of diffusion and erosion of the polymer matrix.[148]

$$\frac{M_t}{M_\infty} = kt^n \tag{4}$$

where M_t/M_∞ is the fractional solute release as the function of time t, k corresponds to the release rate constant, and n is the diffusional exponent for active release. **Table 3** provides the conditions for distinct geometric configurations with varying values of the release exponent "n" which are often overlooked. This can result in incorrect interpretations of the experimental outcomes.[149] The Fickian diffusion model, also known as Case I, is identified by an "n" value of 0.5, where the insect-repellent release is primarily governed by diffusion processes. In contrast, when "n" equals 1, the system exhibits non-Fickian, or Case II transport, characterized by zero-order release kinetics. For values of "n" between 0.5 and 1, the transport model is described as non-Fickian or anomalous, where the substance release is influenced by both diffusion and polymeric chain swelling. Lastly, the Super Case II transport model is denoted by an "n" value greater than 1, representing an extreme form of transport.[149] Figure 12b represents the kinetic modeling (Korsmeyer–Peppas) for the in vitro release of L-Carvone from blend of PCL-WC.[151]

Table 3. Some values of the exponent "n" based on geometry (Phala et al., 2023; Bruschi, 2015).

Mechanism Model	Geometry	Release Exponent (n)
Case I	Planar	0.50
	Cylinders	0.45
	Spheres	0.43
Anomalous	Planar	$0.50 < n < 1.0$
	Cylinders	$0.45 < n < 0.89$
	Spheres	$0.43 < n < 0.85$
Case II	Planar	1.0
	Cylinders	0.89
	Spheres	0.85
Super Case II	Planar	$n > 1$
	Cylinders	$n > 0.89$
	Spheres	$n > 0.85$

6.4. Weibull Model

The Weibull model is a versatile statistical tool commonly applied to describe the release kinetics of active agents from polymeric matrices, including nanofibers used for delivering insect repellents. Unlike models strictly derived from physical laws, the Weibull model is empirical and provides a flexible method for analyzing the data that may not fit conventional release kinetics (Equation (5)).[117,152]

$$M\ (t) = 1 - e^{-\left(\frac{t}{\tau}\right)^{\beta}} \tag{5}$$

where $M(t)$ is the amount of drug released at time t, τ is the scale parameter, which is indicative of the time scale of the process, and β is the shape parameter, which defines the curve's shape, indicating the release mechanism. In addition, the value of the shape parameter β can provide insight into the release mechanism. The adaptability of the Weibull model lies in its ability to fit a wide range of release profiles by adjusting its parameters, making it a robust tool for predicting the release rates of insect repellents from nanofibers.[149] This model can be advantageous in the early stages of formulation development when the precise release mechanisms are not yet fully understood, allowing researchers to approximate the release kinetics and adjust formulation parame-

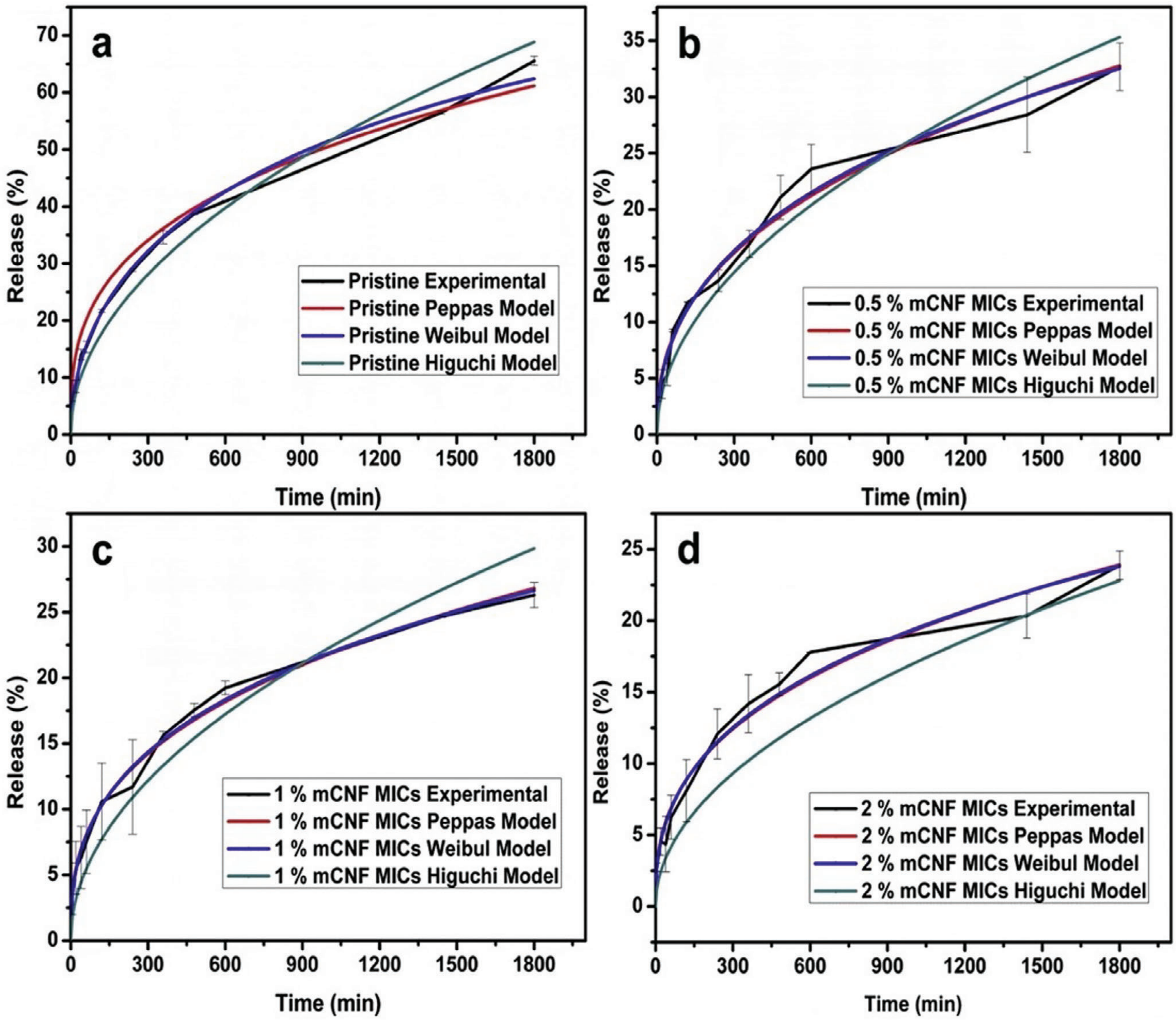

Figure 13. Experimental and predicted release rate of DEET from polyurethane microcapsules (MICs). a) MICs with Hypermer A60. b) MICs with 0.5% stearic acid functionalized cellulose nanofibers (mCNF); c) MICs with 1% mCNF; d) MICs with 2% mCNF. Reproduced (Adapted) with permission.[119] Copyright 2019, Elsevier.

ters accordingly.[153,154] **Figure 13** represents the kinetic modeling for the release of DEET in polyurethane microcapsules, including Weibull model.

6.5. Other Models

In addition to the substance release models already mentioned, such as Higuchi, Korsmeyer–Peppas, and Weibull, other models are widely used in the characterization and prediction of the release behavior of active agents from polymeric systems such as 1) The Baker–Lonsdale model which is an extension of the Higuchi model to spherical systems, such as micro- and nanoparticles.[144] It considers the diffusion of the compound through a homogeneous sphere and is used to describe the release kinetics from systems with spherical geometry; 2) The Hopfenberg model which is based on releasing substances from polymers that undergo erosion.[155] This model is suitable for systems where release is controlled by erosion of the polymer matrix rather than drug diffusion; 3) The Peppas–Sahlin model combines the effects of diffusion and erosion or relaxation of the polymer chain.[156–158] This model helps describe complex systems where diffusion and erosion mechanisms are significant in repellent release; and 4) the Gompertz model, which is empirical and describes the release of substances as a sigmoid function and is often used to represent the absorption and release kinetics of drugs that have an initial slow phase followed by a faster release and then a slowdown (Easton, 2002). Recently, Mapossa et al.[27] developed a new kinetic model and successfully used it to estimate the release rate of insect repellent from polyolefin matrix. The model is based on a simple implicit mechanistic model. Experimental work conducted by Mapossa et al.[27] demonstrated that the model fitted well on the experimental data of linear low-density polyethylene (LLDPE). Furthermore, the model considers quasi-steady state diffusion and a dimensionally stable and inert solid scaffold. This means that it will fail if the polymer absorbs and swells in the presence of the insect repellent. This is expected to be the case for poly(ethylene-co-vinyl acetate (EVA) as this polymer is more polar than polyethylene. Indeed, it is important to note that in some cases the insect-repellent release profiles from EVA matrices were such that they could not be modeled with the Mapossa model, demonstrating that this method fails in swellable polymeric systems.[117]

Finally, these are just a few examples of the many models that can be applied to releasing insect repellents from nanofibers and other polymeric systems. Each model has its assumptions and applications, and the choice of the most appropriate model generally depends on the complexity of the substance delivery system and the release mechanisms involved.

7. Challenges and Future Perspective

In the emerging field of functional textiles for mosquito control, several challenges must be addressed to maximize the effectiveness and viability of products based on electrospun polymeric nanofibers. The question of long-term efficiency is at the heart of the research, as the volatility of repellents requires innovative solutions to stabilize and control their release. Furthermore, the increasing resistance of mosquitoes to current insect repellents is a significant obstacle, requiring continued investment in research to develop new, more effective substances.

The safety and biocompatibility of the materials used are also a priority, as direct and prolonged contact with human skin requires them to be non-toxic and non-irritating. Likewise, it is imperative to consider the environmental sustainability of products, opting for biodegradable polymers and insect repellents that do not harm the environment. In addition to environmental issues, economic aspects, such as the cost and efficiency of scaled production, are crucial for the widespread adoption of these technological innovations.

Looking to the future, research into new polymers and advanced nanotechnology promise to open new possibilities for more efficient, long-acting delivery systems. Customizing functional textiles to meet the specific needs of diverse populations can result in more effective protection against different mosquito species and diseases. Integrating polymeric nanofibers with innovative technologies also presents itself as a promising frontier, enhancing textiles with monitoring and alerting capabilities.

For these advances to materialize and benefit the most affected populations, forming global partnerships between researchers, governments, and international organizations is essential. Education and awareness are crucial in ensuring these new insect repellent textiles' acceptance and appropriate use, especially in underserved communities. By addressing these challenges and seizing future opportunities, electrospinning technology could become a valuable tool in combating mosquito-borne diseases, making a significant impact on global health and social well-being, particularly in regions where malaria and other vector diseases are endemic.

8. Conclusion and Recommendations

Improving mosquito-repellent activity could have a significant impact on combating outdoor mosquito-borne malaria. This work aimed to review studies on fabricating product-based polymeric nanofibers incorporated with insect repellents and evaluating their performance against mosquito bites. Several of the reviewed studies demonstrated that incorporating a mosquito repellent into polymeric nanofibers and utilizing slow release as a practicable and effective technology can control mosquito bites outdoors for weeks or months. These polymeric nanofibers are cost-effectively fabricated using electrospinning technology. This technology may offer an affordable, textile-based, long-lasting insect repellent intervention that can be deployed in disadvantaged communities where malaria is mostly prevalent and endemic. Furthermore, electrospun fibers can be considered as suitable candidate formulations for biomedical applications, particularly in insect-repellent delivery. Electrospinning is a technique that can be scaled up and used on an industrial scale to fabricate nanofiber scaffolds for medical applications. However, knowledge of the properties and the uses of electrospun fibers still needs to be explored and carefully investigated. In addition, products based on polymeric nanofibers with insect repellents should be tested in large-scale field trials to evaluate their impact on reducing malaria transmission particularly in endemic communities. Besides that, more studies on the basic principles of the formation and insect-repellent release mechanism from electrospun nanofibers should be done. Finally, before the products of electrospun-based insect repellents are commercially acceptable, extensive and rigorous entomological and epidemiological studies should be done. Electrospinning technology is a promising tool in the field of medicine and insect-repellent delivery.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

A.B.M. was associated with conceptualization, investigation, methodology, wrote the original draft, formal analysis, validation, and reviewed and edited the final manuscript. A.H.d.S.J. performed investigation, methodology, wrote the original draft, formal analysis, validation, and reviewed and edited the final manuscript. W.M. performed validation, funding acquisition, and reviewed and edited the final manuscript. U.S. performed validation, supervision, funding acquisition, and reviewed and edited the final manuscript. C.R.S.d.O. performed investigation, methodology, wrote the original draft, validation, and reviewed and edited the final manuscript.

Keywords

electrospinning, functional textiles, human health, malaria control, mosquito repellent, release rate

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[1] A. B. Mapossa, W. W. Focke, R. K. Tewo, R. Androsch, T. Kruger, *Malar J.* **2021a**, *20*, 1.
[2] V. Muñoz, F. Buffa, F. Molinari, L. G. Hermida, J. J. García, G. A. Abraham, *Mater. Lett.* **2019**, *253*, 289.
[3] A. Kapesa, E. J. Kweka, H. Atieli, Y. A. Afrane, E. Kamugisha, M. C. Lee, G. Zhou, A. K. Githeko, G. Yan, *PLoS One* **2018**, *13*, e0202031.
[4] J. H. Diaz, *Wilderness Environ. Med.* **2016**, *27*, 153.
[5] V. D. Melo, J. S. Silva, R. L. Corte, *Public Health* **2019**, *171*, 89.
[6] M. F. Maia, S. J. Moore, *Malar J.* **2011**, *10*, 1.
[7] M. M. Specos, J. J. García, J. Tornesello, P. Marino, M. D. Vecchia, M. D. Tesoriero, L. G. Hermida, *Trans. R. Soc. Trop. Med. Hyg.* **2010**, *104*, 653.
[8] C. T. Lim, *Prog. Polym. Sci.* **2017**, *70*, 1.
[9] L. Persano, A. Camposeo, C. Tekmen, D. Pisignano, *Macromol. Mater. Eng.* **2013**, *298*, 504.
[10] M. K. Gaydhane, C. S. Sharma, S. Majumdar, *RSC Adv.* **2023**, *13*, 7312.
[11] Y. Fu, W. J. Kao, *Expert Opin. Drug Deliv.* **2010**, *7*, 429.
[12] K. Vinothini, M. Rajan, In Charact. Biol. Nanomater. Drug Delivery, **2019**, 219.
[13] F. L. He, X. Deng, Y. Q. Zhou, T. D. Zhang, Y. L. Liu, Y. J. Ye, D. C. Yin, *Polym. Adv. Technol.* **2019**, *30*, 425.
[14] J. J. Ryan, R. Casalini, J. A. Orlicki, J. G. Lundin, *Polym. Adv. Technol.* **2020**, *31*, 3039.
[15] A. C. Fulton, M. D. Thum, J. Jimenez, G. Camarella, J. E. Cilek, J. G. Lundin, *ACS Appl. Mater. Interfaces* **2023**.
[16] I. Bonadies, A. Longo, R. Androsch, D. Jehnichen, M. Göbel, M. L. Di Lorenzo, *Eur. Polym. J.* **2019**, *113*, 377.
[17] M. D. Thum, N. K. Weise, R. Casalini, A. C. Fulton, A. P. Purdy, J. G. Lundin, *J. Appl. Polym. Sci.* **2022**, *139*, e53237.
[18] J. Zhang, C. Xiao, X. Zhang, Y. Lin, H. Yang, Y. S. Zhang, J. Ding, *J. Controlled Release* **2021**, *335*, 359.
[19] F. Du, I. Bonadies, A. Longo, H. Rupp, M. L. Di Lorenzo, R. Androsch, *ACS Appl. Polym. Mater.* **2023**, *5*, 4838.
[20] I. Bonadies, A. Longo, R. Androsch, M. L. Di Lorenzo, *AIP Conf. Proc.* **2018**, *1981*.
[21] J. J. Ryan, R. Casalini, J. A. Orlicki, J. G. Lundin, *Polym. Adv. Technol.* **2020**, *31*, 3039.
[22] L. Ciera, L. Beladjal, L. Van Landuyt, D. Menger, M. Holdinga, J. Mertens, L. Van Langenhove, K. De Clerk, T. Gheysens, *R. Soc. Open Sci.* **2019**, *6*, 182139.
[23] I. Y. Prosanov, A. A. Matvienko, *Phys. Solid State* **2010**, *52*, 2203.
[24] M. Sibanda, W. Focke, L. Braack, A. Leuteritz, H. Brünig, N. H. A. Tran, F. Wieczorek, W. Trümper, *Mater. Sci. Eng., C* **2018**, *91*, 754.
[25] E. E. Revay, A. Junnila, R. D. Xue, D. L. Kline, U. R. Bernier, V. D. Kravchenko, W. A. Qualls, N. Ghattas, G. C. Müller, *Acta Trop.* **2013**, *125*, 226.
[26] S. D. Rodriguez, H. N. Chung, K. K. Gonzales, J. Vulcan, Y. Li, J. A. Ahumada, H. M. Romero, M. De La Torre, F. Shu, I. A. Hansen, *J. Insect Sci.* **2017**, *17*, 24.
[27] A. B. Mapossa, M. M. Sibanda, A. Sitoe, W. W. Focke, L. Braack, C. Ndonyane, J. Mouatcho, J. Smart, H. Muaimbo, R. Androsch, M. T. Loots, *Chem. Eng. J.* **2019**, *360*, 435.
[28] F. Du, H. Rupp, K. Jariyavidyanont, A. Janke, A. Petzold, W. Binder, R. Androsch, *Int. J. Pharm.* **2022**, *624*, 122023.
[29] A. C. Fulton, M. D. Thum, J. Jimenez, G. Camarella, J. E. Cilek, J. G. Lundin, *ACS Appl. Mater. Interfaces* **2023**, *15*, 44722.
[30] S. A. S. Chatha, M. Asgher, R. Asgher, A. I. Hussain, Y. Iqbal, S. M. Hussain, M. Bilal, F. Saleem, H. M. Iqbal, *Sci. Total Environ.* **2019**, *690*, 667.
[31] N. L. Achee, J. P. Grieco, H. Vatandoost, G. Seixas, J. Pinto, L. Ching-Ng, A. J. Martins, W. Juntarajumnong, V. Corbel, C. Gouagna, J. P. David, *PLoS Negl. Trop. Dis.* **2019**, *13*, e0006822.
[32] A. Agnihotri, S. W. Ali, A. Das, R. Alagirusamy, In The Impact and Prospects of Green Chemistry for Textile Technology, **2019**, 307.
[33] S. Li, J. E. Lewis, N. M. Stewart, L. Qian, H. Boyter, *J. Textile Inst.* **2008**, *99*, 177.
[34] S. Kala, A. Agarwal, N. Sogan, S. N. Naik, B. N. Nagpal, P. K. Patanjali, J. Kumar, *Colloids Surf., B* **2019**, *181*, 789.
[35] M. Debboun, S. P. Frances, D. Strickman, *Insect Repellents Handbook*, CRC Press, Boca Raton, FL **2014**.
[36] F. F. Céspedes, M. V. Sánchez, S. P. García, M. F. Pérez, *Chemosphere* **2007**, *69*, 785.
[37] A. Akelah, *Mater. Sci. Eng., C* **1996**, *4*, 83.
[38] E. R. Kenawy, D. C. Sherrington, A. Akelah, *Eur. Polym. J.* **1992**, *28*, 841.
[39] A. S. M. Raja, S. Kawlekar, S. Saxena, A. Arputharaj, P. G. Patil, *Int. J. Mosquito Res.* **2015**, *2*, 49.
[40] S. A. Farag, H. Osama, R. Mohamed, H. Mohamed, *Mater. Sci. Appl.* **2011**, *2*, 200.
[41] A. Hebeish, I. A. Hamdy, S. M. El-Sawy, F. A. Abdel-Mohdy, *J. Textile Inst.* **2010**, *101*, 627.
[42] A. Hebeish, I. A. Hamdy, S. M. EL-Sawy, F. A. Abdel-Mohdy, *Res. J. Text. Apparel* **2009**, *13*, 24.
[43] A. Hebeish, M. M. Fouda, I. A. Hamdy, S. M. El-Sawy, F. A. Abdel-Mohdy, *Carbohydr. Polym.* **2008**, *74*, 268.
[44] F. A. Abdel-Mohdy, M. M. Fouda, M. F. Rehan, A. S. Aly, *Carbohydr. Polym.* **2008**, *73*, 92.
[45] J. Banupriya, V. Maheshwari, *J. Textile Sci. Eng.* **2013**, *3*, 123.
[46] J. M. Hougard, S. Duchon, M. Zaim, P. Guillet, *J. Med. Entomol.* **2002**, *39*, 526.
[47] L. Jajpura, M. Saini, A. Rangi, *Colourage* **2016**, 44e48.
[48] M. Ardanuy, M. Faccini, D. Amantia, L. Aubouy, G. Borja, *Surf. Coat. Technol.* **2014**, *239*, 132.
[49] M. Govindarajan, R. Sivakumar, *Asian Pac. J. Trop. Med.* **2011**, *4*, 941.
[50] R. Ramasamy, R. Rajan, R. Velmurugan, *Malaya J. Bio-Sci.* **2014**, *1*, 19.
[51] R. Anitha, T. Ramachandran, R. Rajendran, M. Mahalakshmi, *Elixir Bio. Phys.* **2011**, *40*, 5196.
[52] M. M. Specos, J. J. García, J. Tornesello, P. Marino, M. D. Vecchia, M. D. Tesoriero, L. G. Hermida, *Trans. R. Soc. Trop. Med. Hyg.* **2010**, *104*, 653.
[53] R. Bano, *J. Textile Sci. Eng.* **2014**, *4*, 1.
[54] A. Khalf, S. V. Madihally, *Eur. J. Pharm. Biopharm.* **2017**, *112*, 1.
[55] S. Thakkar, M. Misra, *Eur. J. Pharm. Sci.* **2017**, *107*, 148.
[56] T. Jiang, E. J. Carbone, K. W. H. Lo, C. T. Laurencin, *Prog. Polym. Sci.* **2015**, *46*, 1.
[57] I. Sebe, P. Szabó, B. Kállai-Szabó, R. Zelkó, *Int. J. Pharm.* **2015**, *494*, 516.
[58] A. Repanas, S. Andriopoulou, B. Glasmacher, *J. Drug Deliv. Sci. Technol.* **2016**, *31*, 137.
[59] N. Tucker, J. J. Stanger, M. P. Staiger, H. Razzaq, K. Hofman, *J. Eng. Fiber Fabr.* **2012**, *7*, 155892501200702.
[60] J.-H. He, Y.-Q. Wan, L. Xu, *Chaos, Solitons Fractals* **2007**, *33*, 26.
[61] S. K. Nataraj, K. S. Yang, T. M. Aminabhavi, *Prog. Polym. Sci.* **2012**, *37*, 487.
[62] A. Senthamizhan, B. Balusamy, T. Uyar, *Electrospun Materials for Tissue Engineering and Biomedical Applications*, 1st ed. (Eds.: T. Uyar, E. Kny), Woodhead Publishing, Sawston, UK **2017**, Ch1.
[63] W. E. Teo, S. Ramakrishna, *Nanotechnology* **2006**, *17*, R89.

[64] Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna, *Composite Sci. Technol.* **2003**, *63*, 2223.

[65] R. Akins, J. Rabolt, *Electrospinning Fundamentals and Applications*, 3rd ed., Elsevier, Cham **2013**.

[66] I. S. Chronakis, *Micromanufacturing Engineering and Technology*, 2nd ed. (Ed.: Y. Qin), William Andrew, Norvich, NY **2015**, 513.

[67] P. Davoodi, E. L. Gill, W. Wang, Y. Y. Shery Huang, *Biomedical Applications of Electrospinning and Electrospraying* (Eds.: N. Kasoju, H. Ye), Woodhead Publishing, Sawston, UK **2021**, p. 45.

[68] L. D. Tijing, Y. C. Woo, M. Yao, J. Ren, H. K. Shon, *Electrospinning for Membrane Fabrication: Strategies and Applications*, Elsevier, Cham **2017**.

[69] Y. Liu, M. M. Mohideen, K. Li, S. Ramakrishna, *Melt Electrospinning*, Elsevier, Cham **2019**.

[70] P. D. Dalton, D. Grafahrend, K. Klinkhammer, D. Klee, M. Möller, *Polymer* **2007**, *48*, 6823.

[71] N. Detta, T. D. Brown, F. K. Edin, K. Albrecht, F. Chiellini, E. Chiellini, P. D. Dalton, D. W. Hutmacher, *Polym. Int.* **2010**, *59*, 1558.

[72] P. D. Dalton, D. Klee, M. Möller, *Polymer* **2005**, *46*, 611.

[73] R. Nayak, R. Padhye, L. Arnold, *Electrospun Nanofibers* (Ed.: M. Afshari), Woodhead Publishing, Sawston, UK **2017**, p. 11.

[74] A. Moreira, D. Lawson, L. Onyekuru, K. Dziemidowicz, U. Angkawinitwong, P. F. Costa, N. Radacsi, G. R. Williams, *J. Controlled Release* **2021**, *329*, 1172.

[75] T. D. Brown, P. D. Dalton, D. W. Hutmacher, *Prog. Polym. Sci.* **2016**, *56*, 116.

[76] L. Muthukrishnan, *Colloid Polym. Sci.* **2022**, *300*, 875.

[77] F. Zhao, Y. Liu, H. Yuan, W. Yang, *J. Appl. Polym. Sci.* **2012**, *125*, 2652.

[78] T. D. Brown, P. D. Dalton, D. W. Hutmacher, *Adv. Mater.* **2011**, *23*, 5651.

[79] B. Guan, R. B. Cole, *Encyclopedia of Mass Spectrometry*, Elsevier, Cham **2016**, 132.

[80] L. Cao, J. Luo, K. Tu, L.-Q. Wang, H. Jiang, *Colloids Surf., B* **2014**, *115*, 212.

[81] S. Faraji, B. Sadri, B. Vajdi Hokmabad, N. Jadidoleslam, E. Esmaeilzadeh, *Exp. Therm. Fluid. Sci.* **2017**, *81*, 327.

[82] L. Zhang, J. Huang, T. Si, R. X. Xu, *Expert Rev. Med. Devices* **2012**, *9*, 595.

[83] B. Ding, J. Yu, X. Wang, *Electrospinning: Nanofabrication and Applications*, William Andrew, Norwich, NY **2019**.

[84] D. Gugulothu, A. Barhoum, R. Nerella, R. Ajmer, M. Bechelany, *Handbook of Nanofibers*, Springer, Berlin **2019**, 45.

[85] E. Kostakova, L. Meszaros, J. Gregr, *Mater. Lett.* **2009**, *63*, 2419.

[86] H. Niu, T. Lin, *J. Nanomater.* **2012**, *2012*, 725950.

[87] R. Chen, J. Liu, Z. Sun, D. Chen, *Nanofabrication* **2018**, *4*, 17.

[88] G. H. Kim, H. Yoon, *Appl. Phys. A Mater. Sci. Process* **2008**, *90*, 389.

[89] H. Hsiao, C. Huang, Y. Liu, Y. Kuo, H. Chen, *J. Appl. Polym. Sci.* **2012**, *124*, 4904.

[90] M. Pokorny, V. Rassushin, L. Wolfova, V. Velebny, *Polym. Eng. Sci.* **2016**, *56*, 932.

[91] X. Wang, I. C. Um, D. Fang, A. Okamoto, B. S. Hsiao, B. Chu, *Polymer* **2005**, *46*, 4853.

[92] Y. Lin, Y. Yao, X. Yang, N. Wei, X. Li, P. Gong, R. Li, D. Wu, *J. Appl. Polym. Sci.* **2008**, *107*, 909.

[93] G. C. Dadol, A. Kilic, L. D. Tijing, K. J. A. Lim, L. K. Cabatingan, N. P. B. Tan, E. Stojanovska, Y. Polat, *Mater. Today Commun.* **2020**, *25*, 101656.

[94] Z. Huang, C. He, A. Yang, Y. Zhang, X. Han, J. Yin, Q. Wu, *J. Biomed. Mater. Res., Part A* **2006**, *77A*, 169.

[95] M. F. Elahi, W. Lu, *J. Bioeng. Biomed. Sci.* **2013**, 3.

[96] Z. Sun, E. Zussman, A. L. Yarin, J. H. Wendorff, A. Greiner, *Adv. Mater.* **2003**, *15*, 1929.

[97] J. Yoon, H. Yang, B. Lee, W. Yu, *Adv. Mater.* **2018**, *30*.

[98] X. Qin, *Electrospun Nanofibers* (Ed.: M. Afshari), Woodhead Publishing, Sawston, UK **2017**, p. 41.

[99] Y. Lu, J. Huang, G. Yu, R. Cardenas, S. Wei, E. K. Wujcik, Z. Guo, *Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol.* **2016**, *8*, 654.

[100] Y. Zhao, X. Cao, L. Jiang, *J. Am. Chem. Soc.* **2007**, *129*, 764.

[101] M. Kamperman, L. T. J. Korley, B. Yau, K. M. Johansen, Y. L. Joo, U. Wiesner, *Polym. Chem.* **2010**, *1*, 1001.

[102] H. Zhang, X. Qin, J. Wu, Y.-B. He, H. Du, B. Li, F. Kang, *J. Mater. Chem. A* **2015**, *3*, 7112.

[103] C. R. Martin, P. Kohli, *Nat. Rev. Drug Discov.* **2003**, *2*, 29.

[104] N. Wang, Y. Zhao, *Electrospinning: Nanofabrication and Applications*, Elsevier, Cham **2019**, 125.

[105] X. Wang, H. Niu, X. Wang, T. Lin, *J. Nanomater.* **2012**, *2012*, 785920.

[106] Y. Li, Y. Wan, Y. Zhang, J.-H. He, P. Wang, *Thermal Science* **2016**, *20*, 993.

[107] J.-H. He, *Recent Pat. Nanotechnol.* **2020**, *13*, 162.

[108] D. Tian, C.-J. Zhou, J.-H. He, *Text. Res. J.* **2019**, *89*, 1340.

[109] F. I. Bell, I. J. McEwen, C. Viney, *Nature* **2002**, *416*, 37.

[110] H.-J. Jin, D. L. Kaplan, *Nature* **2003**, *424*, 1057.

[111] J.-H. He, Y. Liu, L. Xu, J.-Y. Yu, G. Sun, *Chaos, Solitons Fractals* **2008**, *37*, 643.

[112] Y. Liu, J.-H. He, J.-Y. Yu, *J. Phys.: Conf. Ser.* **2008**, *96*, 012001.

[113] D. Sun, C. Chang, S. Li, L. Lin, *Nano Lett.* **2006**, *6*, 839.

[114] N. Bhardwaj, S. C. Kundu, *Biotechnol. Adv.* **2010**, *28*, 325.

[115] J. D. Schiffman, C. L. Schauer, *Polym. Rev.* **2008**, *48*, 317.

[116] X. You, C. Ye, P. Guo, *J. Manuf. Processes* **2017**, *30*, 431.

[117] A. Sitoe, A. B. Mapossa, W. W. Focke, H. Muiambo, R. Androsch, J. Wesley-Smith, *SPE Polymers* **2020**, *1*, 90.

[118] World Health Organization, *World Malaria Report World Health Organization*, WHO, Geneva, Switzerland **2022**.

[119] S. L. Kadam, P. Yadav, S. Bhutkar, V. D. Patil, P. G. Shukla, K. Shanmuganathan, *Colloids Surf. A* **2019**, *582*, 123883.

[120] R. Manjula, S. Rajiv, *Polym.-Plast. Technol. Eng.* **2017**, *56*, 1949.

[121] W. Zhang, Z. He, Y. Han, Q. Jiang, C. Zhan, K. Zhang, Z. Li, R. Zhang, *Compos. Part A Appl. Sci. Manufac.* **2020**, *137*, 106009.

[122] N. Devi, J. Dutta, *Int. J. Biol. Macromol.* **2017**, *104*, 1897.

[123] R. Venturelli, A. P. Immich, S. Souza, A. A. Souza, *J. Appl. Polym. Sci.* **2021**, *138*, 50258.

[124] A. H. da Silva Júnior, D. L. P. Macuvele, H. G. Riella, C. Soares, N. Padoin, *J. Environ. Chem. Eng.* **2021**, *9*, 105728.

[125] A. Singh, J. Sheikh, *Carbohydr. Polym.* **2022**, *290*, 119466.

[126] M. R. M. da Silva, E. Ricci-Júnior, *Acta Trop.* **2020**, *212*, 105419.

[127] A. C. Fulton, M. D. Thum, J. Jimenez, G. Camarella, J. E. Cilek, J. G. Lundin, *ACS Appl. Mater. Interfaces* **2023**, *15*, 44722.

[128] T. J. Lopes, G. R. Rosa, G. A. Fernandes, C. W. Scheeren, A. H. da Silva Júnior, M. L. Martins, *Protective Textiles Nat. Res.* **2022**, 649.

[129] C. R. S. de Oliveira, A. H. da Silva Júnior, A. P. S. Immich, J. Fiates, *Mater. Lett.* **2022**, *316*, 132047.

[130] K. Iliou, S. Kikionis, P. V. Petrakis, E. Ioannou, V. Roussis, *Pest Manage. Sci.* **2019**, *75*, 2142.

[131] J. J. Ryan, R. Casalini, J. A. Orlicki, J. G. Lundin, *Polym. Adv. Technol.* **2020**, *31*, 3039.

[132] A. Raman, J. S. Jayan, B. D. S. Deeraj, A. Saritha, K. Joseph, *Surfaces Interfaces* **2021**, *24*, 101140.

[133] S. Konchada, N. Killi, S. Sayyad, G. B. Gathalkar, R. V. N. Gundloori, *RSC Adv.* **2020**, *10*, 42827.

[134] N. Lv, M. Zhao, L. Hao, X. Zhou, H. Chen, H. Zhou, *Ind. Crops Prod.* **2022**, *190*, 115902.

[135] A. R. Almeida, N. D. Oliveira, F. A. S. D. Pinheiro, W. A. de Morais, L. D. S. Ferreira, *Pestic. Biochem. Physiol.* **2023**, *195*, 105538.

[136] F. Pardini, Á. Iregui, P. Faccia, J. Amalvy, A. González, L. Irusta, *Int. J. Polym. Anal. Charact.* **2021**, *26*, 497.

[137] A. P. B. Balaji, A. Ashu, S. Manigandan, T. P. Sastry, A. Mukherjee, N. Chandrasekaran, *J. King Saud. Univ. Sci.* **2017**, *29*, 517.
[138] J. D. Ogilvie-Battersby, R. Nagarajan, R. Mosurkal, N. Orbey, *Colloids Surf. A* **2022**, *640*, 128494.
[139] D. dos Santos, A. M. Oliveira, N. N. P. Cerize, K. C. Manhani, D. Santos, H. C. de Araujo, S. A. Costa, S. M. Costa, *Mater. Chem. Phys.* **2022**, *280*, 125662.
[140] F. Du, I. Bonadies, A. Longo, H. Rupp, M. L. Di Lorenzo, R. Androsch, *ACS Appl. Polym. Mater.* **2023**, *5*, 4838.
[141] C. Xiang, N. R. Etrick, M. W. Frey, E. J. Norris, J. R. Coats, *Polymers* **2020**, *12*, 2196.
[142] C. R. S. de Oliveira, A. H. da Silva Júnior, J. Mulinari, A. P. S. Immich, *Sustain. Prod. Consumption* **2021**, *28*, 1232.
[143] C. R. S. de Oliveira, P. V. de Oliveira, L. Pellenz, C. R. L. de Aguiar, A. H. da Silva Júnior, *J. Environ. Sci.* **2023**, *140*, 123.
[144] M. H. Shoaib, S. A. S. Siddiqi, R. I. Yousuf, K. Zaheer, M. Hanif, S. Rehana, S. Jabeen, *AAPS PharmSciTech* **2010**, *11*, 708.
[145] A. B. Mapossa, J. López-Beceiro, A. Díaz-Díaz, R. Artiaga, D. Moyo, T. Mphateng, W. Focke, *Molecules* **2021b**, *26*, 5890.
[146] Y. Fu, W. J. Kao, *Expert Opin. Drug Deliv.* **2010**, *7*, 429.
[147] D. Samaha, R. Shehayeb, S. Kyriacos, *Dissolution Technol.* **2009**, *16*, 41.
[148] J. Siepmann, *Adv. Drug Deliv. Rev.* **2001**, *48*, 139.
[149] M. L. Bruschi, *Strategies to Modify the Drug Release from Pharmaceutical Systems*, Woodhead Publishing, Sawston, UK **2015**.
[150] A. Valério, E. Mancusi, F. Ferreira, S. M. A. Guelli Ulson de Souza, A. A. U. de Souza, S. Y. G. González, *Eur. Polym. J.* **2019**, *112*, 400.
[151] M. Ramamoorthy, S. Rajiv, *Carbohydr. Polym.* **2015**, *133*, 328.
[152] K. Kosmidis, P. Argyrakis, P. Macheras, *J. Chem. Phys.* **2003**, *119*, 6373.
[153] A. B. Mapossa, A. Sitoe, W. W. Focke, H. Izadi, E. L. du Toit, R. Androsch, C. Sungkapreecha, E. M. van Der Merwe, *Pest Manage. Sci.* **2020**, *76*, 1112.
[154] T. N. Mphateng, A. B. Mapossa, J. Wesley-Smith, S. Ramjee, W. W. Focke, *Cellulose* **2022**, *29*, 3915.
[155] P. Trucillo, *Processes* **2022**, *10*, 1094.
[156] A. Talevi, M. E. Ruiz, *ADME Encyclopedia*, Springer, Berlin **2021**.
[157] D. M. Easton, *Pharm. Res.* **2002**, *19*, 463.
[158] K. Phala, A. B. Mapossa, W. Augustyn, S. Combrinck, B. Botha, *Arabian J. Chem.* **2023**, *16*, 104458.

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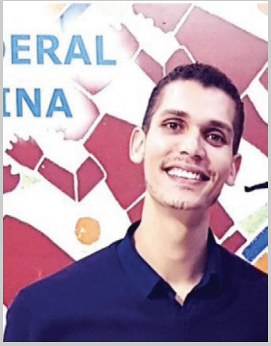

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