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Biobased Polymer Resources and Essential Oils: the Green Combination for Antibacterial Applications

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To fight nosocomial infections, the excessive use of antibiotics has led to the emergence of multidrug resistant microorganisms which are now considered as a relevant public health threat by the World Health Organization. To date, even through most of the antibacterial systems lie in the use of petro-sourced polymers depleting thus the natural global supplies, and silver NPs are widely accepted to be the most active biocide against a wide range of bacteria strains, the toxicity issues and the growing interest for natural products have gained increasing interest since the last decade. Therefore, the design of performing antibacterial materials derived from biomass remain a fantastic challenge for scientific community. Attention has then shifted to naturally occurring substances such as essential oils (EOs), which are classified as Generally Recognized as Safe (GRAS). EOs could offer an alternative to the common antimicrobial agents, as an inner solution or as a biocide agent to inhibit the resistance mechanism. Herein, the review not only aims at providing a state of the art of the antibacterial modes of action of EOs against various bacterial strains, the recent advances in genomic and proteomic techniques for the elucidation of these mechanisms, but also gives examples of biobased polymer resources based EOs materials and their resulting antibacterial activities. Especially, the antibacterial properties of biobased polymers e.g. cellulose, starch, chitosan, PLA PHAs and proteins, associated with EOs (cinnamon (CEO), clove (CLEO), bergamot (BEO), ginger (GEO), lemongrass (LEO), caraway (CAEO), rosemary (REO), *Eucalyptus globulus* (EGEO), tea tree (TTEO), orange peel (OPEO) and apricot (*Prunus armeniaca*) kernel (AKEO) essential oils) are described. Finally, discussions on the influence of EOs on the mechanical strength of the bio-based materials are also evoked

Introduction

Nosocomial infections cause each year millions of deaths all over the world. Indeed, in the U.S. about more than 2.8 million of patient suffer from an antibiotic-resistant infection, and 35,000 people die, for an estimated national cost of more than $4.6 billion annually[1]. To overcome this issue, the use of excessive quantity of antibiotics was the general strategy. However, this has rapidly led to the emergence and spread of multidrug resistant microorganisms which are now considered as a relevant public health threat by the World Health Organization. For instance, *Staphylococcus aureus* and *Pseudomonas aeruginosa* represent a serious threat and are responsible for more than 50% of the global nosocomial infections as they created resistance to antibiotics. The rising of antibiotics resistance of bacteria makes some of them totally unefficient. Although Vancomycin was considered as a bulkwark to treat nosocomial infections, some Vancomycin resistant bacteria have nowadays emerged[2]. Therefore, the development of new antibacterial materials is of great importance to prevent adhesion and proliferation of hazardous pathogens responsible for these infections. Other pathogens such as Acinetobacter, Klebsiella, E. coli, Serratia and Proteus can also provoke serious infections such as bloodstream infections and pneumonia.

Thus, novel antibacterial materials or surfaces are designed to address the nosocomial infections according to different mechanisms of action[3-7] proposed in literature: i) the anti-fouling strategy, ii) the contact-killing approach, iii) the biocide-release strategy and iv) the photoinactivation of bacteria method. Antifouling surfaces were generally synthesized from polyethylene glycol (PEG) or oligo (ethylene glycol) and to a lesser extent with zwitterionic or superhydrophobic polymers[8]. PEG chains impart adhesion resistance to proteins thus limiting bacterial adhesion on PEG-modified surfaces[9-10]. The contact-killing approaches commonly implied cationic polymers bearing lethal functional groups e.g. quaternary ammonium moieties, antimicrobial peptides and derivatives, antimicrobial enzymes and polycations, to pathogens by contact[5]. In the biocide-release strategy, preloaded biocidal agents are slowly released from the materials to induce bacterial death. The most commonly used biocidal agents include metal oxide nanoparticles (TiO_2, ZnO)[11], silver NPs[7, 12-13] and nitrogen oxide[14-15]. Finally, bacteria photoinactivation method uses light

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to generate reactive oxygen species within the materials[16-21], leading to bacterial death.

Most of the antibacterial systems lie in the use of petro-sourced or non-renewable polymers depleting thus the natural global supplies. Therefore, the design of performing antibacterial materials derived from biomass remain a fantastic challenge. Meanwhile, the global current policies towards green sustainable chemistry have imposed to chemical industries to reorient their strategies for synthesizing biobased products from renewable resources[22]. Consequently, the interest in renewable chemistry has tremendously grown in the last decade. Scientist community focused their attention on biobased polymers extracted from vegetables, cereals, invertebrate animals, plants or microorganisms[23-25]. However, pre-treatments *e.g.* purification, chemical or enzymatic modifications, are generally needed to access pure molecules usable in the synthesis of materials. To date cellulose, starch, chitosan, and poly(lactic acid) (PLA) are widely used and easily affordable due to low cost production. Cellulose is considered as the most abundant compound extracted from biomass and was used since centuries as a raw material [26-27]. Each year, the worldwide production of cellulose is estimated to be around 1011 tons. Starch is considered as the most abundant renewable, natural and biodegradable polysaccharide and is the most commonly employed raw materials because of its high availability, the easiness to handle and its low costs[28]. According to ReportLinker the global market for starch is estimated to reach 156.3 million metric tons by 2025[29]. Also, chitosan is obtained from alkaline hydrolysis of chitin which is considered as the second most abundant natural polymer found in Nature[30], the first being cellulose. PLA is biotechnologically synthesized by direct fermentation of metabolically engineered bacteria or by enzymatic catalysis[31-32]. Globally, the PLA market reached $ 535.6 million in 2019 and is expected to rise up 15.9% in the next ten years. Notably, Polyhydroxyalkanoates (PHAs) are also promising bio-based polymers due to their inherent biocompatibility, biodegradability, and environment-friendly properties[33]. Despite the high production costs of PHAs, promising extraction processes with reduced costs have led to an increase in the number of investigations on the subject for the last decade.

Today, even through silver NPs have been widely accepted to be the most active biocide against a wide range of bacteria strains, the toxicity issues and the growing interest for natural products have been put to the forefront. Attention has then shifted to naturally occurring substances such as essential oils (EOs), which are classified as Generally Recognized as Safe (GRAS)[34]. EOs extracted from plants are composed of biologically active compounds such as terpenes or phenolic derivatives, and some of them are recognized to have antibacterial properties[35-36]. EOs could offer an alternative to the common antimicrobial agents, as an inner solution or as an agent to inhibit the resistance mechanism. Nevertheless, a perfect knowledge of the composition and the mode of action of each different component is required before expecting a systemic clinical use.

Therefore, this review not only aims at providing a state of the art of the antibacterial modes of action of EOs against various bacterial strains, but also gives examples of biobased polymer resources based EOs materials and their resulting antibacterial activities. In the first part are described the two main reported mode of action of different EOs against bacteria cell membrane. We also report the recent advances in genomic and proteomic techniques for the elucidation of these antibacterial mechanisms. In the second part, an overview of the biobased polymer resources based Essential Oils materials is provided, in particular, attention will be paid on the antibacterial properties of biobased polymers *e.g.* cellulose, starch, chitosan, PLA, PHAs and proteins, associated with EOs (cinnamon, clove, bergamot (BEO), ginger (GEO), lemongrass (LEO), caraway (CAEO), rosemary (REO), e*ucalyptus globulus* (EGEO), tea tree (TTEO), orange peel (OPEO) and apricot (*Prunus armeniaca*) kernel (AKEO), thyme (TEO) and oregano (OREO) essential oils). Discussions on the influence of EOs on the mechanical strength of the bio-based materials will be also evoked.

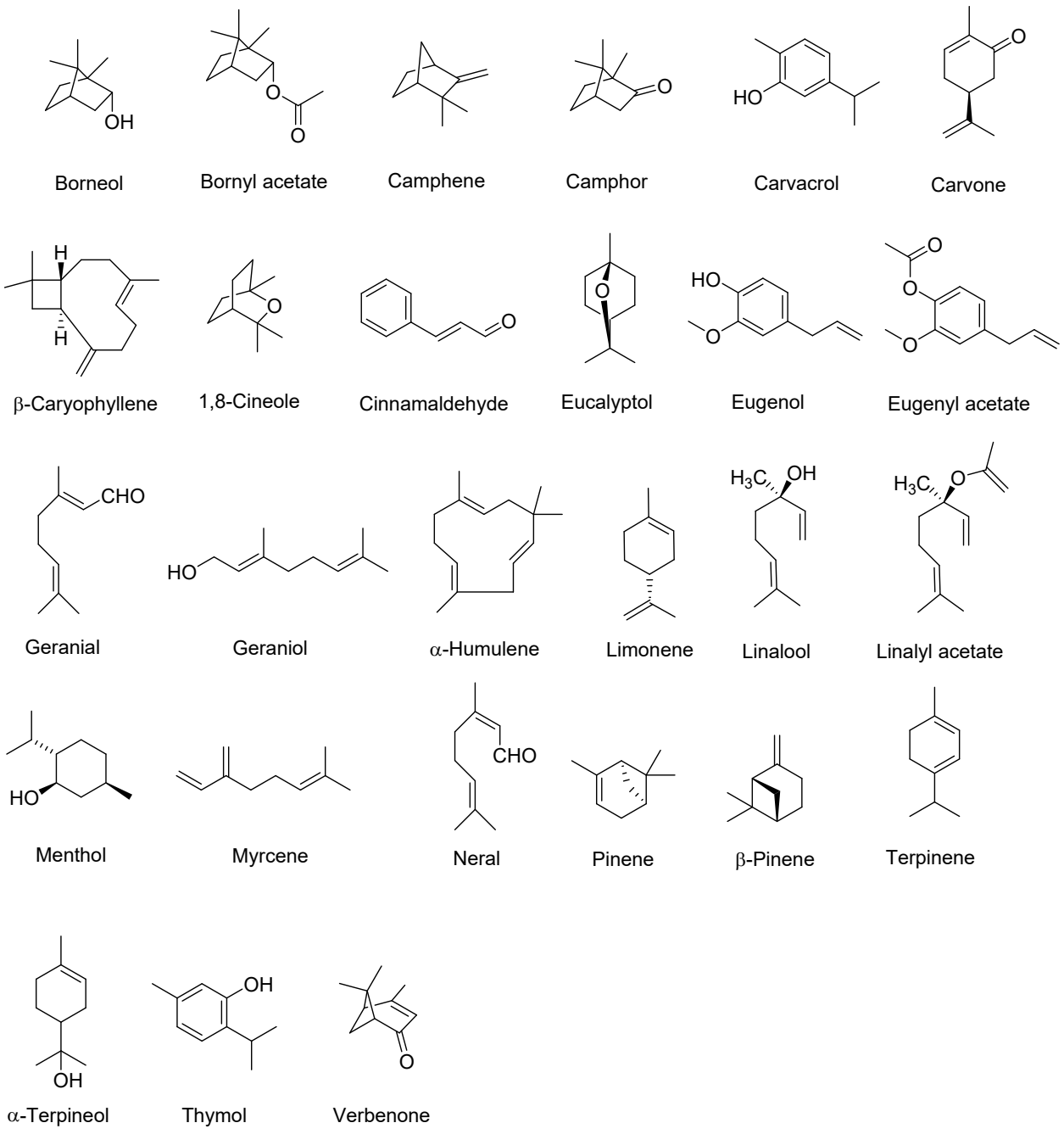
1. Essential Oils: Compositions and Antibacterial Mechanisms

Essential oils (EOs) are composed of a mixture of volatile and lipophilic molecules which are extracted from plants by different extraction methods (hydro-, dry distillation or mechanical extraction techniques)[35, 37-38]. Chemical compositions of EOs change according to geographic places, storage time and conditions, extraction techniques, botanical sources, and parts of the plants used during extraction (whole fruit, stems, leaves, roots, seeds) increasing the difficulties to compare the mode of actions of different EOs[36]. Globally, EOs contain various chemical molecules with outstanding antibacterial activities such as polyphenols, terpenes, aldehydes, ketones, alcohols, ethers[39]. Focusing on compounds that have been studied in bio-based polymers, terpenes are the most predominant chemical compound family that exhibited antibacterial activities. The chemical structures of the main active component of essential oils are displayed in Scheme 1. They could be sub classed as:

- Cyclic monoterpene: Carvacrol (5-isopropyl-2-methylphenol), L-Carvone, D-limonene, Terpinene-4-ol, Thymol (2-isopropyl-5methyl phenol)
- Diterpene: Carnosic acid
- Linear monoterpene: *Trans*- Geraniol, Linalool

The second important chemical compound family is the phenylpropanoid class divided as follow:

  - *Trans*-Cinnamaldehyde
  - Eugenol (2-methoxy-4-(prop-2-en-1-yl) phenol) and Isoeugenol (2-methoxy-4-(prop-1-en-1-yl) phenol



Scheme 1. Chemical structures of the main active components found in essential oils.

The main active compounds present in the EOs described in this review (cinnamon, clove, bergamot, ginger, lemongrass, caraway, rosemary, e*ucalyptus globulus*, tea tree, orange peel and apricot (*Prunus armeniaca*) kernel EOs) and their common applications are described in Table 1.

Table 1. Major active compounds of essential oils (EOs)

EOs	Major active compounds	Applications
Apricot (*Prunus armeniaca*) kernel EOs		
Apricot (*Prunus armeniaca*) kernel EO from New Zealand[40]	Oleic acid (69.0%), linoleic acid (26.0%)	Thermal energy storage[41], cosmetic products[42], food products[43], introduced in the formulation of bakery and confectionery products[44]
Bergamot EOs		
Bergamot EO produced in Reggio Calabria[45]	Limonene (37.2%), linalyl acetate (30.1%), linalool (8.8%), *γ*-Terpinene (6.8%) and β-pinene (6.2%)	Used by perfume industries for enhancing the flagrance[46]. Used by pharmaceutical industries to capture unpleasant smells from medicines[46]. Used as a flavor in food industries[46]. Used in medicine as antimicrobial agent for wound healing and for treating upper respiratory-tract problems and hyperhidrosis[46]. Used in aromatherapy to facilitate sleep and stress disorders[47].
Bergamot EO produced in Italy[48] (Messina)	Limonene (42.8%), linalyl acetate (27.14%), linalool (5.55%), *γ*-Terpinene (6.19%) and β-pinene (5.59%)	
Caraway EOs		
Caraway EO from different countries[49]	Carvone (44.5-95.9%) and limonene (1.5-51.3%)	Used in medicine[50] for the antispasmodic, stimulant, stomachic and tonic properties, and for its colon cancer chemo-preventive action[51]. Used also in food[50, 52] as a flavouring of cheese, chewing gums, candies, meat products. Used in cosmetics, toothpaste, and some pharmaceutical preparations[50]
Clove EOs		
Clove leaf essential oil (Eugenia caryophyllus)[53]	Eugenol (76.8%), β-Caryophyllene (17.4%), α-Humulene (2.1%), eugenyl acetate (1.2%)	Used as food preservatives[54] (baked foods, dairy products) while maintaining nutritional value and sensory characteristics. Used as packaging materials[54] and in biological applications[54] (Anticancer, analgesic, anti-coagulant, anti-inflammatory, antimicrobial…).
Cinnamon EOs		
Cinnamon EO from *Cinnamomum cassia* leafs[55]	*Trans*-Cinnamaldehyde (30.36%), o-Methoxy-cinnamaldehyde (25.39%), 3-Methoxy-1,2-propanediol (29.30%)	Used in medicine to treat gastritis, blood circulation problems and inflammatory diseases[56]. Cinnamon EOs are also used as spice and flavouring agent for foods[57].
Cinnamon EO from *Cinnamomum zeylanicum* leafs[55]	Eugenol (79.75%), *trans*-Cinnamaldehyde (16.25%)	
Cinnamon EO from *Cinnamomum tamala* leafs[55]	5-(2-Propenyl)-1,3-benzodioxole (28.67%), *trans*-Cinnamaldehyde (15.90%), α-Terpineol (12.59%), Borneol (11.95%), 2-Methoxy-3-(2-propenyl)-phenol (10.68%)	
Cinnamon EO from *Cinnamomum burmannii* leafs[55]	*Trans*-Cinnamaldehyde (60.17%), eugenol (17.62%), coumarin (13.39%)	
Cinnamon EO from *Cinnamomum pauciflorum* leafs[55]	Eugenol (54.74%), 5-(2-Propenyl)-1,3-benzodioxole (17.23%), *trans*-Cinnamaldehyde (12.80%),	
***Eucalyptus globulus* EOs**		

Eucalyptus globulus EO from Monastir, Tunisia[58]	1-8 Cineole (95.61%), α-Pinene (1.50%)	Used in medicine[59] for the treatment of respiratory problems, as anti-inflammoratory, antimicrobial, antioxidant, analgesic and anticancer agents. Used in dermatological applications[60-61] for reducing aging skincare
Lemongrass EOs		
Lemongrass (*Cymbopogon citratus*) EO from Algeria[62-63]	Geranial (42.16%), neral (31.52%), myrcene (7.45%)	Used in medicine[64] to control blood pressure or to treat digestive problems. Used in pharmaceutical industries[64] thanks to its anti-depressant, analgesic, antipyretic, bactericidal and astringent properties.
Lemongrass (*Cymbopogon citratus*) EO from Saudi Arabia[63, 65]	Geranial (37.80%), neral (33.60%), myrcene (8.40%)	
Lemongrass (*Cymbopogon citratus*) EO from Zambia[63]	Geranial (39%), neral (29.40%), myrcene (18%)	
Oregano EOs		
Origanum vulgare L. ssp. viride growing in Iran[66]	Thymol (29.90%), γ-Terpinene (13.0%), β-Pinene (11.30%)	Used in the biomedical fields[67-68], cosmetics and food preservation[68] as antimicrobial, antifungal and antioxidant agents.
Origanum vulgare L. in different countries[69-70]	Carvacrol (2,30-95,00%), thymol (0,20-90,20%), *p*-Cymene (1,88-15,80%) and γ-Terpinene (0,10-24,45%)	
Orange peel EOs		
Orange peel EO from Uganda[71]	Limonene (89.7%), myrcene (2.4%), sabinene (1.6%), linalool (1.2%)	Used in food industries[72] for food preservation, antimicrobial packaging and as flavouring agent in drinks and ice creams. Used in cosmetic industries[72] : addition in perfumes, deodorants and shampoos. Used in pharmaceutical industries[72] due to its anti-inflammatory properties.
Orange peel EO from Rwanda[71]	Limonene (92.5%), myrcene (2.2%), α-Pinene (2.4%), linalool (0.9%)	
Orange peel EO from central - eastern Sicily and cultivated at the University of Palermo[73]	Limonene between 73.9 and 97.6% and discrete % of linalool, geraniol and as α-Terpineol	
Ginger EOs		
Ginger from Northeast Region of India[74]	Geraniol (6.41-52.79%), z-Citral (0.86-42.13%), eucalyptol (1.4-18.46%), camphene (0-15.25%)	Used essentially in food preservation industries[75]
Rosemary EOs		
Rosemary EO (*Rosmarinus officinalis L.*) from the subtropical region of north India[76]	Camphor (23.9-35.8%), 1,8-Cineole (18.0-23.9%), α-Pinene (4.5-14.4%), verbenone (6.5-12.4%), camphene (2.5-6.9%), limonene (2.1-2.8%), bornyl acetate (1.1-4.1%), α-Terpineol (1.9–3.6%) and β-Pinene (2.1–3.3%)	Used in flagrance cosmetic industries[77] for the elaboration of bath essences, hair lotions and shampoos. Used in food industries[78] as flavouring agent. Used in medicine[79] due to its antioxidant properties, its antirheumatic effect and enhancing blood-circulation of the limbs.
Tea tree EOs		
Tea tree EO from Carros, France[58]	Terpinen-4-ol (40.44%), γ-Terpinene (19.54%), α-Terpinene (7.69%), 1,8-Cineole (5.20%)	Used in medicine for the treatments of herpes, acne, bacterial infections[80]
Tea tree EO from Australia[81]	Terpinen-4-ol (40.1%), γ-Terpinene (23%), α-Terpinene (10.4%), 1,8-Cineole (5.10%)	
Thyme EOs		
Thymus vulgaris EO cultivated in Romania[82]	Thymol (47.59%), γ-Terpinene (30.90%), *p*-Cymene (8.41%)	Used in medicine[83] against respiratory infections, symptoms of bronchitis or as an expectorant in cough. Used in dentistry[84] as disinfectant due to its antibacterial, antifungal and antioxidant properties.
Albanian thyme (*Thymus vulgaris L.*) EO[86]	*p*-Cymene (7.76-43.75%), γ-Terpinene (4.20-27.62%), thymol (21.38-60.15%), carvacrol (1.15-3.04%) and β-Caryophyllene (1.30-3.07%)	

		Used in food industries[85] for increasing shelf-life periods of foods.

Essential oils (EOs) have low toxicity, low cost and are widely used in pharmaceutical, cosmetic, food and beverage industries, as well as for antibacterial applications. For this later, the presence of hydrophilic functional groups and the lipophilicity characteristic of EOs favor their antibacterial activities. EOs demonstrated to be active antibacterial compounds against several pathogens such as *Escherichia coli*, *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Bacillus subtilis*, *Enterococcus faecalis*, *Enterococcus faecium*, *Salmonella typhi*, *Shigella dysenetriae*, *Shigella flexneri*, *Acinetobacter baumannii*, *Klebsiella peneumoniae* [36]. Notably, Gram-positive bacteria are reported to be more sensitive to EOs than that of Gram-negative one as they offer a weak resistance to the penetration of hydrophobic compounds. Indeed, the peptidoglycan layer of the Gram-negative bacteria is associated with a complex outer membrane which is formed by a double layer of phospholipids and lipopolysaccharides [87].

Although the *in vitro* antimicrobial activities of numerous EOs have been widely demonstrated, the entire mechanism of action remains unclear. The first reason is that EOs are a mixture of individual compounds which themselves putatively present different antibacterial mode of action. Secondly, most of experimental approaches consist in biochemical assays that not specific enough to identify accurately the target(s): stain- or fluorescence-based efflux assay, ion efflux essay, measure of the membrane surface charge, electron microscopy. Nevertheless, the two main reported mode of action are the disruption of the bacterial membrane and the transport system. First genomics data including gene expression (reverse transcriptase PCR, microarray…) and proteomic analysis underlined (i) the overexpression of oxidative stress-related proteins and reactive oxygen species, and (ii) the decreasing of oxidative stress-sensitive proteins, that promote lipid peroxidation and membrane disruption[88-89]. The proteomic data confirmed the dramatic decrease of proteins originated from the membrane or the cytoplasm that support the membrane disruption. Besides the intracellular linkage as a consequence of membrane disruption, the occurrence of reactive species leads to irreversible damages of protein and genetic material [90]. Until data from genomics specify the mode of antibacterial action of each active component, published data reported the structure – activities relationship of some particular compounds.

Traditionally, the antibacterial modes of EOs action are their capability to disrupt bacterial membranes. For example, Cox et al. reported that tea tree essential oils favour intracellular material leakage and potassium ion efflux in *E. coli* and *S. aureus* structures[91]. The lavender essential oils strongly modify the zeta potential of the *E. coli* membrane, phenomenon which is associated with the membrane disruption, increasing thus the permeability of the membrane. These findings have been corroborated by microscopy analyses which evidenced the modification of cell structure and morphology[92]. In light of these considerations, Zhang et al. reported similar results with the use of black pepper essential oil against *E. coli* [93]. Interestingly, Yang et al. also proved by zeta potential measurement and scanning electron microscopy, that cinnamon EOs have a great antibacterial efficiency against *K. pneumoniae* by disrupting its membrane[94].

Regarding terpenes, the role of hydroxyl groups in certain position of phenolic rings, double bonds, and delocalized electrons seem to be significant. As for an example, the carvacrol activity could be due to the presence of a free phenolic hydroxyl substituent that allow the crossing of the bacteria membrane and the binding of ATP or monovalent cations [95]. Once exporting out of the cell, the membrane potential and the homoeostasis is impaired, leading to the cell membrane rupture. The activity of thymol seems to be due to the presence of phenolic hydroxyl groups and the contribution of the phenolic ring that bind to membrane and periplasmic space proteins through hydrogen bonding and hydrophobic interactions [95]. The incorporation into the polar-head group region of the lipid bilayer impaired the fluidity and then the integrity of the membrane. Additionally, and among the representative of the phenylpropanoid class, the *trans*-Cinammaldehyde is reported to modify the lipid profile of the bacterial membrane, increasing the presence of saturated fatty acids[96]. This action increases the rigidity of the membrane, leading to the depolarization and the loss of membrane integrity.

The second postulated mechanism of antibacterial actions concern the inhibition of the efflux system of bacteria. The efflux system consists in channel proteins on the bacterial membrane which allow the removal of toxic compounds from the intracellular environment of bacteria. For instance, the efflux inhibition activity of three *Salvia* species against *Staphylococcus epidermis* was investigated by Chovanová et al.[97]. Interestingly, the addition of EOs increases the antibiotic susceptibility of *Staphylococcus epidermis*. Similar activity was observed with *eucalyptus* EO against *K. pneumoniae, S. aureus,* and *Moraxella catarrhalis.* Recently, Espinoza et al. highlighted the synergistic effect of *heartwood* essential oil and antibiotic on the efflux activity of toxic molecules in *S. aureus* : as a consequence, the concentration of antibiotics used against bacteria growth significantly dropped down[98].

Despite the increasing investigations on the mode of EOs action against bacteria strains, there is still a lack of knowledge of the exact antibacterial mechanisms. Therefore, and due to the recent advances in genomic and proteomic techniques, the elucidation of these mechanisms in the next decade is highly probable. The comparison of the gene expression between treated and non-treated EOs cells is the best way to identify the mode of action of EOs. For instance, Myszka et al determined that the lagella-related gene flgA which regulate quorum sensing activity is under expressed when adding thyme EO[99]. Kovács et al. evidenced the increase in expression of oxidative stress response genes in *Campylobacter jejuni* with *peppermint* essential oil contact[88]. Lai et al reported that the membrane damage of *E. coli* is associated to the increase expression of phosphotransferase system and lipopolysaccharide biosynthesis genes[100].

As previously mentioned, proteomic analysis may also help to identify proteins signals generated from bacteria when in contact with EOs. Kovács et al. demonstrated that the treatment of *Campylobacter jejuni* with *peppermint* essential oil induced the over expression of oxidative stress proteins such as *dps, sodB*, and *katA* [88]. In a similar way, around 15 oxidative stress-related proteins were detected in *Salmonella enteritidis* cell membrane upon contact with oregano essential oil[89]. The same trend is observed when cinnamon bark essential oil is put into contact with *K. pneumoniae* cells [94]. More precisely, LC-MS/MS investigation on *K. pneumoniae* has highlighted an increase in the oxidative stress-sensitive proteins such as glycyl radical cofactor, catalase peroxidase and DNA mismatch repair protein, indicating a disruption of the cell membrane by lipid

peroxidation during cinnamon bark essential oil treatment. A complementary study reported the proteome profile of untreated and lavender EOs-treated *K. pneumoniae* which revealed a significant decrease of NADH-quinone oxidoreductase, protein A from the outer membrane, ATP synthase, and cytoplasmic proteins associated to the cell membrane disruption[101]. As a conclusion, EOs induce oxidative stress resulting in the lipid peroxidation of bacterial membrane, its leakage and eventually its death. Even if comparative studies of the antibacterial properties between EOs and other common antibacterial agents such as inorganic nanoparticles (NPs), positively charged molecules/polymers are not easy as numerous different experimental conditions are used to synthesize materials in literature, some authors have studied the synergistic antimicrobial activities of EOs and silver NPs or antibiotics. For instance, cinnamaldehyde, demonstrated a strong synergistic activity when combined with Ag NPs against spore-forming *Clostridium perfringens* and *Bacillus cereus*[102]. Bacterial analysis highlighted an acceleration of the bactericidal action exerted by this combination, leading to an extensive damage of the cell envelope. Thymol and carvacrol, both major active components of OREO and TEO, showed synergism with ampicillin, tetracycline, penicillin, bacitracin, erythromycin and novobiocin against *Salmonella Typhimurium*[103]. Also, the association thymol (or cinnamaldehyde) and ampicillin, tetracycline, penicillin, erythromycin or novobiocin leads to a significant reduction of *Escherichia coli*[103]. According to time-kill studies, the combination of CLEO or eugenol with ampicillin or gentamicin has revealed a 4-16-fold reduction of the number of oral bacteria[104] (*S. mutans, Streptococcus sanguinis, S. sobrinus, Streptococcus ratti, Streptococcus criceti, Streptococcus anginosus, Streptococcus gordonii, A. actinomycetemcomitans, Fusobacterium nucleatum, Prevotella intermedia, and Porphylomonas gingivalis*). Rosato et al. verified the antibacterial effectiveness of four EOs (*Aniba rosaeodora, Melaleuca alternifolia, Origanum vulgare (OREO), and Pelargonium graveolens)* individually associated with gentamicin against 15 different Gram positive and Gram negative bacteria[105]. The *in vitro* association *Aniba rosaeodora*/gentamicin and *Pelargonium graveolens*/Gentamicin were effective against Gram negative bacteria, and particularly with *Acinetobacter baumannii*. Similar results were observed by combining coriander *(Coriandrum sativum L.)* EO and six antibacterial drugs (cefoperazone, chloramphenicol, ciprofloxacin, gentamicin, tetracycline and piperacillin) against *Acinetobacter baumannii*[106]. Also, the *in vitro* association TTEO/tobramycin against *Escherichia coli* and *Staphylococcus aureus* permits to significantly increase the post-antibiotic effect and is of interest for the development of new conjunctiva and respiratory infection treatments[107]. Interestingly, in order to move towards green chemistry, and reduce both the use of petro-sourced materials and the bacterial resistance to antibiotics, the combination of EOs with natural polymers is a great alternative.
In the next section, many examples of biobased polymer resources associated with EOs are further reported and their corresponding antibacterial activity against different pathogens is described.

2. Synthesis methodology and Antibacterial Testing Methods of Biobased Polymer Resources based Essential Oils Materials.

The preparation of natural polymers-based essential oils and the antibacterial testing methods will be first reported following by the description of the antibacterial activities of the resulting bio-based films. The synthesis of bio-based films need at least the introduction of three compounds *e.g.* natural biopolymer, solvent and a plasticizer (glycerol or sorbitol are the most frequently used). In addition, the mixture with other biopolymers is sometimes envisaged to tune properties of the films. In this context, the introduction of essential oils (EOs) will ensure the antibacterial activities of the films. However, most of the mentioned natural biopolymers used to synthesize films or coatings have a hydrophilic nature which strongly restricts the loading of hydrophobic EOs. To overcome this restriction and to broaden the synthesis of antibacterial films associated with natural bioactive EOs, emulsification casting method and electrospinning technique have been addressed. Compression is also employed to develop and optimize the properties of the films as described below.

2.1. Preparation Methods of the natural polymer-based essential oils films.

Natural polymers based EOs materials are essentially processed using three main techniques: emulsification casting method, electrospinning, and compression.

2.1.1. Emulsification casting method

The most commonly used method for the synthesis of natural polymers based EOs remains the solvent/emulsification casting technique due to its easiness and the use of economical equipment (Figure 1). This method consists in pouring a formulation into a small plate (or a petri dish) followed by a slow evaporation of the solvent (usually water) under drying. However, as EOs are poorly soluble in water, emulsification is often applied to overcome this problem. Emulsification is considered as an attractive method to enhance stability and dispersion of EOs in aqueous systems, hence ensuring prolonged antibacterial activities[108]. This method has been extensively employed with cellulose derivatives[109], starch[110], gelatin[111] or chitosan[112]. As the stability of EO droplets in emulsions by natural polymer presence have not been solely demonstrated, therefore the addition of surfactants or combination with other processing methods are mandatory. Most of the recent investigations used Tween 80 (or polysorbate 80) as an emulsifier[113-114], glycerol (or sorbitol) as a plasticizer[115], and the ultrasonication is implemented to decrease the EO droplet sizes, favouring the emulsion stability[116]. The authors agree that the surface of hydrophobic EOs are enriched by hydrophilic fragments of the emulsifier, enhancing their stability in water medium[114, 117]. In a lesser extent, β-cyclodextrins were also used to promote EOs solubility in aqueous medium[118] and pre-encapsulation of EOs was also suggested by Jiang et al.[119].

In a final step, after heating at low temperature (30-50°C), the film forming solution is casted on flat Teflon film-coated glass plates and dried at room temperature[120-122]. Interestingly, the control of the film thickness is managed through the mass of the poured formulation. Mixing times and temperatures are both significant parameters which ensure homogeneous dispersion of components into polymer matrix.

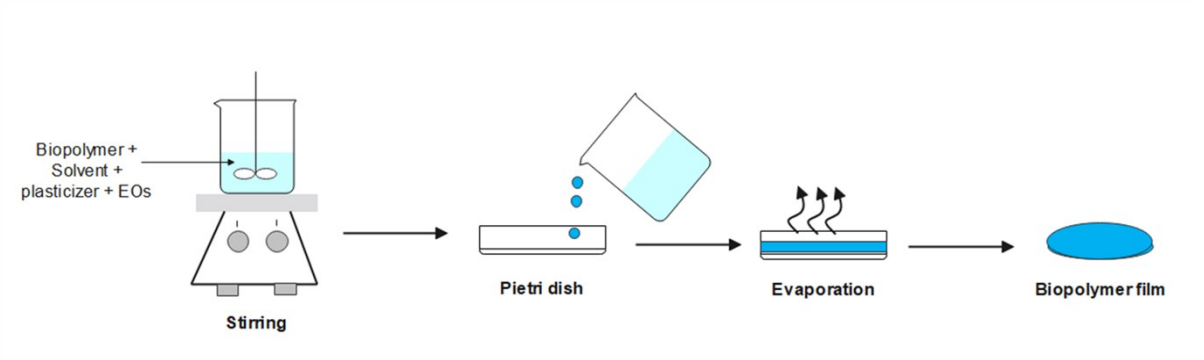


Figure 1. Procedure for the formation of a biopolymer film according to the emulsification casting method.

2.1.2. Electrospinning (ES)

Electrospinning has attracted great attention since decades as a versatile process to produce micro-/nano-fibers with high porous structures and high surface-to-volume ratio according to an electrohydrodynamic process. Many interesting reviews have described in detail this method. As illustrated in Figure 2, the electrospinning set-up is rather simple, and can be accessible to all laboratories[123-124]. The main components of ES include a syringe pump, a high-voltage power supply (either a direct current or alternating current), a spinneret, and a conductive collector. Basically, the electrospinning technique can be divided into four consecutive steps: (i) accumulation of charges within a polymer solution and formation of a cone-shaped jet from the capillary tip; (ii) extension of the charged jet along an uniaxial thin line and solvent evaporation; (iii) thinning of the jet with the electric field and increase of electrical bending instability; and (iv) collection of the jet as solid micro- or nano-fiber(s) on the grounded collector. Two sets of parameters influence the morphology of the electrospun fibers[125]: a) the intrinsic parameters (solution viscosity, solvent evaporation rate, and conductivity of the polymer solutions) and b) the processing parameters (voltage, feeding rate, collector shape and distance to the collector).

Due to the high specific surface area, electrospun fibers have an edge in encapsulation efficiencies and highlighted great potential for applications involving the controlled release of active molecules, while exhibiting biodegradability and biocompatibility. Although the incorporation of EOs into fibers was demonstrated earlier, no investigation has reported the application of electrospun-loaded EOs for antimicrobial materials until 2014[126]. Within the last few years, polyvinyl alcohol[127], chitosan[126], polycarbonate[128], and polyethylene oxide[129] have been widely applied for encapsulating EOs (cinnamon, limonene, clove and oregano essential oils) through electrospinning because of their excellent properties for the synthesis of fibers[130], and it have been shown that electrospun fibers promoted long-term efficiency when used for the encapsulation of antimicrobial agents[126, 129]. However, despite the encapsulation enhances the stability and solubility of EOs, their hydrophobicity and volatility make them difficult to be directly introduced into the electrospinning solution. Therefore, the addition of carrier substances[131-133] such as cyclodextrins, liposomes, or chitosan is usually required.

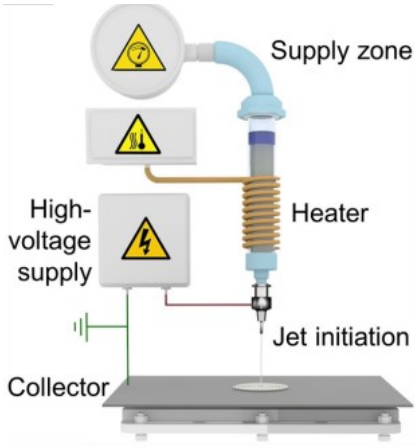


Figure 2. Schematic illustration of a setup for electrospinning a polymer melt onto a static collector[134]. Reprinted with permission from ref 80. Copyright 2019 American Chemical Society.

2.1.3. Compression moulding[135-136]

The incorporation of EOs in biodegradable films leads to high losses of volatiles when materials are made, either in the casting method or according to a thermo-process method (extrusion or melt blending). Therefore, Requena et coworkers have developed an interesting strategy for improving the process for the synthesis of EOs-derived films based on the spraying of EOs on one side of a film and the subsequent thermo-compression of both films, leading to a bilayer film with the active compounds at the interface[135].

Interestingly, the poly[(3-hydroxybutyrate)-*co*-(3-hydroxyvalerate)] (PHBV) monolayers have been sprayed with a known amount of EOs (oregano essential oil (OREO), carvacrol (CA), clove essential oil (CLEO) or eugenol (EU)) with respect to the PHBV matrix and covered with another PHBV monolayer. Both monolayers were subsequently compressed at the melting temperature of PHBV at high pressure (7 MPa) followed by a cooling cycle.

2.2. Antibacterial testing methods of the natural polymer-based essential oils.

Many methods for evaluating the antibacterial properties of materials have been described in literature. Some of them are more suitable for enumerating live bacteria attached to material surface and others for determining the lowest concentration of biocide agent that completely inhibits the growth of microorganisms. The following section does not aim at exhaustively describing the overall antibacterial testing methods but only ones commonly employed with natural polymer based essential oils. Therefore, the agar diffusion and the counting methods are the most appropriate ones to screen or quantively estimate the antibacterial efficiency of the synthesized materials. Both methods have been routinely used to rapidly evaluate the antibacterial activities of natural polymer based essential oils.

2.2.1. Agar disk and well diffusion methods

The agar disk-diffusion method is officially used in many laboratories for the routine antibacterial tests. However, this method is not accurate enough to detect fastidious bacteria and cannot be employed to determine the minimum inhibitory concentration, as the concentration of biocide agents which diffuse into the agar medium is impossible to quantify. Nevertheless, the agar disk-diffusion method offers many striking advantages over other methods as its simplicity, its low cost, the capability to test multiple bacteria strains and antimicrobial agents, and the simplicity in interpreting the results. In this well-known method, agar plates are inoculated with a standardized microorganism solution. The disc containing the molecule to test at a defined concentration, is deposited on the agar surface. Under suitable incubation conditions, antibacterial agents diffuse from the disk to the agar medium and inhibit the growth of the studied bacteria. According to the diameter of the inhibition zone, one can conclude about the antibacterial efficiency of the biocide agents (Figure 3). The aforementioned advantages of the agar disk-diffusion method make it particularly appropriate for the antibacterial screening of plant extracts and essential oils [137-138]. Similarly to the procedure described for the agar disk-diffusion method, the agar well diffusion method is preferentially used to determine the antimicrobial properties of plant liquid extracts [139-140]. A determined volume of the microbial inoculum is spread on the entire surface of the agar plate. A hole with a defined diameter within the range 6 and 8 mm is done on the center of the agar plate, where a volume (20–100 mL) of the extract solution is introduced at the desired concentration. After incubation in optimal conditions, an inhibitory zone may be observed as previously explained for the disk-diffusion method.

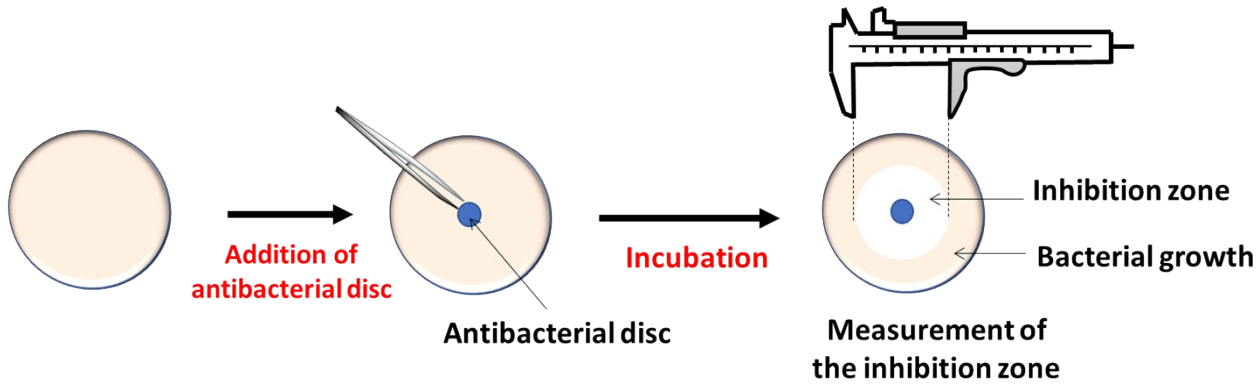


Figure 3. Agar disk diffusion method

2.2.2. The counting method

The counting method is properly used to quantify the number of alive bacteria on the surface of antibacterial materials (Figure 4). Prior to *in vitro* antibacterial tests, the desired bacterial strain is grown overnight in Luria–Bertani (LB) broth at 37 °C under stirring. The corresponding overnight cultures are diluted in sterile LB broth to obtain an OD_{600nm} at 0.05. Standardized samples are immersed in the culture and incubated in optimal conditions according to the bacteria strains used. Following adhesion, samples are rinsed seven times with sterile saline solution (NaCl, 0.9% w/v) to remove any non-adherent or dead bacteria. Cleaned samples are then transferred into 2 ml sterile saline solution and sonicated for 3 min to detach the viable bacteria from the surface of the samples. A 100 µL volume of this solution is then introduced on the surface of a Plat Count agar plate. This process is repeated as many times as there are dilutions. Finally, the total amount of viable bacteria is determined by counting the Colony Forming Units, after 24h or 48h of incubation of the agar plates at 37 ° C, and levels of adhesion are given as numbers of bacteria/cm^2.

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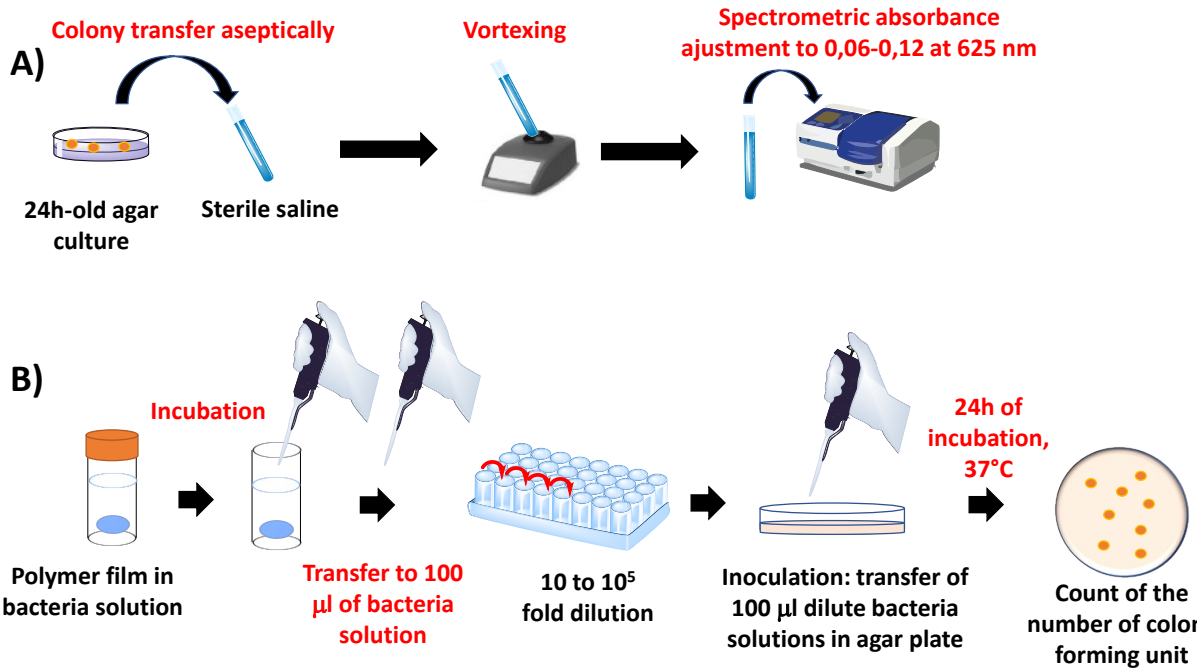

Figure 4. Different steps for the evaluation of alive bacteria according to the counting method.

3. Antibacterial properties of Biobased Polymer Resources based Essential Oils Materials.

Polymers which are produced by the living bodies *i.e.* plants, microorganisms or insects are called natural biopolymers. In this section, we will focus on the association of essential oils with carbohydrate polymers[141-143] (starch, chitosan, cellulose), polyhydroxybutyrate (PHB) and its derivatives)[144], polylactic acid[145] and proteins for the synthesis of new bio-based materials for antibacterial applications.

3.1. Cellulose-based Essential Oil Materials

Cellulose (Figure 5) is considered as the most abundant compound extracted from biomass, especially wood, water plants or agricultural residues. This biopolymer was used since centuries as a raw material. Each year, the worldwide production of cellulose is estimated to be around 10^{11} tons including 6 x 10^9 tons for paper, textile, and chemical industries[26-27]. Cellulose was first extracted from plant matter by a French Chemist (Anselme Payen) in 1839. Nowadays, cellulose and its physical properties no longer holds any secrets. Cellulose is a polysaccharide consisting of a linear chain of several hundreds to over thousands of linked glucose units with the formula $(C_6H_{10}O_5)_n$. The degree of polymerization (DP) for cellulose chains varies respectively from 10,000 to 15,000 for cellulose found in nature and for native cellulose in cotton[27]. Cellulose is successfully extracted from wood, flax, hemp, sisal or cotton, and its extracted amount varies from plant to plant and depends on soy condition. In order to purify cellulose from plants, cellulose should be separated from lignin and hemicelluloses from which physical and chemical bounds exist.

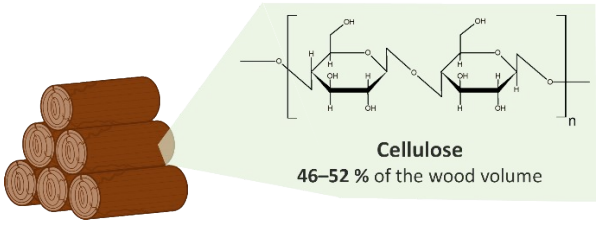

Figure 5. Natural cellulose resources.

In its native form, cellulose has extensive hydrogen bonds that renders difficult its processability. The hydrogen-bonded chemical structure of cellulose makes it insoluble in organic solvents and water. As a result, most of the reactions implying cellulose are performed in solid or swollen state as heterogeneous reactions. For this purpose, reactions are widely carried out in specific solvents such as *N, N*-dimethylacetamide/lithium chloride (DMA/LiCl) and dimethyl sulfoxide/tetrabutylammonium fluoride (DMSO/TBAF) for hydrogen bond disruption[146]. However, and prior to using cellulose, pre-treatment of cellulose is essentially considered for its modification[147]: three approaches *i.e.* enzymatic pre-treatment,

TEMPO-mediated oxidation pre-treatment and carboxymethylation/acetylation process, have been therefore put to the forefront to obtain cohesive and less stiff fibers without any impurities following by post-treatments. From the prospective of applications, post-treatment is essential for the synthesis of new bio-based materials. Chemical modifications using silylation process or acetylation reaction was commonly employed to synthesize new cellulose derivatives which are easier to work with and appear as a real alternative for the synthesis of new materials. Hence, carboxymethyl cellulose (CMC) remains the main extracted compound derived from cellulose using alkaline process. CMC has been successfully used in drug delivery systems, as scaffolds for tissue engineering applications, as renewable materials for bone and dental regeneration and is useful in a wide range of applications in food industry[148]. For instance, the release of apomorphine, a drug which controls motor responses in Parkinson's disease, has been successfully introduced in CMC powder formulation to be used as an efficient delivery vehicle[149]. Sodium CMC was also used in gastrointestinal drug delivery[150]. Apart from drug delivery, CMC appeared as an interesting scaffold for tissue engineering applications. Indeed, as CMC hydrogels present pH-dependent swelling properties, they can lead to the release of drug at the right pH into the tissue of interest in wound dressing materials[151]. Also, CMC hydrogels may encapsulate cells of nucleus pulposis to replace intervertebral disk degeneration[152]. Finally, CMC can be associated with chitosan[153] or hydroxyapatite[154] for bone and dental regeneration applications

However, CMC does not have any antimicrobial properties, and few investigations have showed great potential of CMC in combination with other natural polymers and essential oils as wound dressing and antibacterial materials (Table 2). For this purpose, Rafati et al designed nano-emulsion-base edible films from hydroxypropyl methyl cellulose and containing thymol, carvacrol and *p*-Cymene as essential oils[155]. The addition of EOs influences not only the Young Modulus values of the films but also reveals a plasticizing effect (Table 2). Hence, the high interactions between the hydroxyl groups of EOs and polymer chains increase film flexibility and could be reasonably used as antibacterial materials. Evaluation of the antimicrobial activity of the hybrid films have been done against five Gram positive (*Staphylococcus aureus* (ATCC 25923), *Staphylococcus epidermidis* (ATCC 1435), *Bacillus subtilis* (ATCC 465), *Enterococcus faecalis* (ATCC 29212), *Enterococcus faecium* (clinical strain)), six Gram negative (*E. coli* (ATCC 25922), *Salmonella typhi* (PTCC 1609), *Shigella dysenetriae* (PTCC 1188), *Shigella flexneri* (PTCC 1234), *Acinetobacter baumannii* (Clinical strain), *Klebsiella peneumoniae*) strains and a fungus (*Candida albicans* strain, ATCC 10231) using disk diffusion method. The antibacterial assessments exhibited the highest percentage of bacterial death (against Gram positive) with films containing the highest amount of *p*-Cymene. On the contrary, the edible films with a high amount of thymol and carvacrol demonstrate a high antibacterial activity against Gram negative bacteria. Thymol and carvacrol are expected to disrupt the outer membrane of Gram negative bacteria as revealed by Burt et al.[156]. Results are similar with gelatin-CMC based Bane essential oil[157]. Indeed, 0.8 wt% of EO was necessary to entirely inhibit the growth of *Escherichia. coli*, *Salmonella enterica*, *Staphylococcus aureus*, and *Clostridium sporogenes* according to the agar diffusion method. Interestingly, the subsequent addition of Bane essential oil on gelatin-CMC films has significantly reduced the tensile strength (TS) and therefore increased the flexibility of the films (Table 3).

Na-CMC is also a kind of anionic polysaccharide derived from cellulose, which is not only described as an interesting substrate for edible films but also widely employed in emulsifiers, adhesives, thickeners, and protective colloids in the food and agricultural industries[158]. For instance, Na-CMC was associated with pectin, okara soluble dietary fibers and thyme essential oil (TEO) to successfully synthesize films from waste resources. Not surprisingly, TEO-based films promoted interesting antibacterial activities against Gram-positive bacteria (*S. aureus*, ATCC 25923) and Gram-negative bacteria (*E. coli*, ATCC 25922)[159] along with an increase of the antioxidant activities of the films. On the contrary, authors explained that the increase of pectin concentration decreases bacterial inhibition area by providing essential nutrients for bacterial growth.

Table 2. Antibacterial properties of CMC and cellulose based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Hydroxyl propyl methyl cellulose (HPMC) films	Thymol, carvacrol and *p*-Cymene	*Staphylococcus aureus, Staphylococcus epidermidis, Bacillus subtilis, Enterococcus faecalis, Enterococcus faecium, Escherichia coli, Salmonella typhi, Shigella dysenetriae, Shigella flexneri, Acinetobacter baumannii, Klebsiella peneumoniae*	Agar disk diffusion method	155
Edible coating of gelatin-CMC	Bane essential oil	*Escherichia coli, Clostridium Sporogenes, Salmonella enterica, Staphylococcus aureus*	Agar disk diffusion method	157

Na-CMC/TEO-based films	Thyme essential oil	*Staphylococcus aureus, Escherichia coli*	Agar disk diffusion method	159

Table 3. Mechanical properties of CMC and cellulose based EOs films

Film material	*Tensile strength (MPa)*	*Elongation at break*	*Refs*
Hydroxyl propyl methyl cellulose (HPMC) films	**Without EO** 36.2 ± 0.7 MPa **Wild EO** 19.3 ± 1.0 MPa **Cultivated EO** 22.6 ± 0.7 MPa	**Without EO** 14.1 ± 0.4 cm **Wild EO** 9.02 ± 0.3 cm **Cultivated EO** 14.2 ± 0.04 cm	155
Edible coating of gelatin-CMC with Bane essential oil (BANEO)	**Without BANEO** 5.5 MPa **0.3% of BANEO** 4.5 MPa **0.6% of BANEO** 4.0 MPa **0.8% of BANEO** 3 MPa	-	157
Na-CMC/TEO-based films	**With 0.5% of pectin and without TEO** 6.567 ± 0.33 MPa **With 0.5% of pectin and with 0.1% of TEO** 19.018 ± 1.85 MPa	**With 0.5% of pectin and without TEO** 16.67 ± 0.35 % **With 0.5% of pectin and with 0.1% of TEO** 4.34 ± 0.12 %	159

3.2. Starch-based Essential Oil Materials

Starch is considered as the most abundant renewable, natural, and biodegradable polysaccharide and is the most commonly employed raw materials because of its high availability, the easiness to handle and its low costs. Starch is a component of cereals, roots, seeds, tubers, fruits and vegetables and its properties widely depend on botanical origin, cultivation area and climate[28, 160]. Thanks to its biocompatibility and biodegradability, starch is used in the fabrication of edible films for food packaging. In 2011, in the European Union, 57% of the produced starch was converted to sweeteners i.e. glucose (syrups), fructose (syrups), and polyols such as mannitol, sorbitol and maltitol. Native starch which corresponds to 23% of the global starch production was used in food industries for modifying the texture and consistency of food products[161-162]. The world production of starch is essentially based on corn, cassava, wheat and potatoes, and more than 75% of this production is coming from maize [163]. According to ReportLinker the global market for starch is estimated to reach 156.3 million metric tons by 2025 [29].

Industrial production of starch depends on its botanical origins and its isolation from maize, cassava, wheat, potato or rize requires different industrial methods which have been recently described by Waterschoot et al.[164]. For instance, maize starch is commercially isolated from bulk mass after a multiple step procedure involving steeping in water with sulphur dioxide, followed by wet milling, centrifugation or sedimentation and drying. In the same way, starch is isolated from cassava roots after the removal of impurities by decantation, extraction, followed by centrifugation and drying. On the other hand, starch is extracted from wheat flour and separated from gluten proteins by different techniques, i.e. dough-ball, batter, dough-batter and high pressure disintegration processes [165] which have been extensively described by Van Der Borght et al.[166]. Potatoes starch is separated from non-starch polysaccharides by sieving and centrifugation, then dried by rotating vacuum drum filters [167]. Finally, in rice, starch and proteins which are strongly associated, are separated by alkaline procedure since NaOH solubilises rice proteins and allows the isolation of starch during the wet milling.

Starch is a semicrystalline natural polymer which is predominantly composed of 70-85% of amylopectin, while amylose represents 15 to 30%[28]. Because of intra-/inter-molecular hydrogen bonds between the hydroxyl groups along the polysaccharide chains, starch remains poorly soluble in water and in most of the common organic solvents. Strategies of starch modifications have been

therefore developed to overcome these inconveniences. In the past decades, investigations on starch modifications have been promoted in ionic liquids and supercritical carbon dioxide through regioselective functionalization of hydroxyl groups, the control grafting of starch by living radical polymerizations, reversible addition-fragmentation chain transfer, nitroxide-mediated polymerization, "click" and chemo-enzymatic techniques. This opened new opportunities for the synthesis of new starch derived materials and expand its applications to films and foams production for packaging, drug carrier and medical areas. Particularly, interesting active antimicrobial films have been designed to inhibit the growth of pathogenic microorganisms using starch derivatives in combination with EOs (Table 4). The later was effective against a multitude of microorganisms such as *Listeria monocytogenes* [168-170], *Staphylococcus aureus* [110, 168, 171-174], *Salmonella enterica* [169, 174], *Escherichia coli* [110, 170, 172-174], *Trichoderma harzianum* [172], *Penicillium expansum* [175], *Bacillus cereus* [172], *Enterobacter s.* [172], *Pseudomonas aeruginosa* [172], *Botryodiplodia theobromae Pat.*[176], *Leuconostoc mesenteroides* [177], *Pseudomonas fluorescens* [177] and *Shewanella putrifaciens*[177]. In most of the investigated cases, the increase concentration of EOs promotes the inhibition of bacterial growth. For example, the release of orange essential oil (OEO) from starch derived films with the concentrations of 0.3, 0.5, and 0.7 $\mu L \cdot g^{-1}$ have reduced the *Listeria monocytogenes* development by 68, 80, and 83%, and the *S. aureus* growth by 40, 51, and 66%, respectively. J.A. do Evangelho et al. also demonstrated that the gradual release of OEO allows to maintain antimicrobial activities for a longer period due to D-limonene, the main active compound of OEO[168]. Similar results were obtained with cinnamon essential oil (CEO) and nano titanium dioxide (TiO_2-N) incorporated in sago starch films[178]. The inhibition zones of CEO and TiO_2-N based starch films increase with the CEO and TiO_2-N % contents, while demonstrating thus a more efficient antimicrobial activity against gram positive bacteria (*S. aureus*, and *S. typhi*) than gram negative ones (*E. coli*). TiO_2-N promote the formation of oxidative reactive oxygen species leading to the lipid peroxidation of the cell membrane. On the contrary, cinnamaldehyde, the main hydrophobic and active component of CEO, is known to disrupt bacteria membrane causing bacterial death[179-181]. The antimicrobial results are in accordance with the investigation of Li which highlighted the tremendous inhibition of sodium starch octenylsuccinate (SSOS)-based CEO emulsions against *E. coli* (gram negative), *S. aureus* (gram positive) and *B. subtilis* (gram positive) *via* bacteriostatic interactions between CEO emulsion droplets and bacteria[182]. Antibacterial trends against *Staphylococcus aureus* (Gram-positive bacteria), four Gram-negative bacterial strains *i.e Escherichia coli*, *Pseudomonas aeruginosa*, *Enterobacter sp*, *B. cereus*, as well as *Trichoderma* (fungal strain) are similar to those previously described with millet starch-based films incorporated different concentrations of clove essential oils[172]. The diffusion and release of clove essential oils (CLEO) from film lead to strong antibacterial activities while the inhibitory effect increases with CLEO percentage content. Eugenol, eugenyl acetate and β- caryophyllene, three main active components of CLEO, modify protein structure and cell membrane phospholipids by changing their permeability favouring cell damage, leaching and ion exchange, finally causing cell death[183-184].

In addition to these results, interesting antioxidant activities are generally observed with CEO since cinnamaldehyde, o-methoxycinnamaldehyde, β-caryophyllene-1,8-eucalyptol, dihydroeugenol, and eugenol contained in CEO are known to scavenge free radicals in films increasing thus their lifetime [185]. Significant antioxidant activities have been also observed in CLEO due to the presence of phenolic components, such as Eugenol, Caryophyllene or Humulene considered as radical scavengers [186-187]. In this regard, phenolic compounds which could be found in EOs can inhibit the formation of free radicals by providing a hydrogen atom from their -OH groups [188-189].

Interestingly, the addition of EOs into the materials modify their mechanical properties (Table 5). The tensile strength (TS) and the elongation at break (EB), the key indicators of the strength and flexibility of the films respectively, are described on Table 4. According to Table 4, the addition of oregano EOs negatively impact TS and EB[168-170]. Increasing the concentration of OEO makes the starch materials more fragile, the movement of polymer chains is disfavoured, decreasing thus the flexibility of the materials. Such a trend is also described in G. Al-Hashimi's investigation[172] with CEO. This phenomenon observed on TS is similar than that observed by Ghasemlou et al.[173] when adding *Zataria multiflora Boiss* (ZEO) or *Mentha pulegium* (MEO). In contrast to the previous observations, EB significantly increases when increasing EO content: authors attributed this phenomenon by a reduction of the starch network cohesion which subsequently decreases the films resistance to breakage.

Table 4. Antibacterial properties of Starch-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Cassava starch + processed pumpkin residue extract (PRE) + oregano essential oil (OREO)	Oregano essential oil (OREO)	*Listeria monocytogenes, Staphylococcus aureus, Escherichia coli*	Agar disk diffusion method	170

Corn starch films + Orange essential oil (OEO)	Orange essential oil (OEO)	*Listeria monocytogenes, Staphylococcus aureus, Bacillus cereus, Salmonella typhimurium, Escherichia coli, Shigella dysenteriae, Pseudomonas aeruginosa*	Agar disk diffusion method	168
Starch + Oregano (OREO) or thyme (TEO) essential oil	Oregano essential oil (OREO) or thyme (TEO) essential oil	*Listeria monocytogenes, Salmonella enterica, Escherichia coli*	Agar disk diffusion method	169
Starch + Zataria multiflora Boiss (ZEO) or Mentha pulegium (MEO)	*Zataria multiflora Boiss* (ZEO) or *Mentha pulegium* (MEO)	*Staphylococcus aureus, Escherichia coli*	Agar disk diffusion method	173
Cassava starch + cinnamon essential oil + sodium bentonite clay nanoparticles	Cinnamon essential oil (CEO)	*Staphylococcus aureus, Salmonella enterica, Escherichia coli*	Counting method	174
Cassava starch + PBAT + oregano essential oil (OREO) encapsulated or free	Oregano essential oil (OREO)	*Staphylococcus aureus*	Agar disk diffusion method	171
Starch films + clove essential oil (CEO)	Clove essential oil (CLEO)	*Staphylococcus aureus, Escherichia coli, Trichoderma harzianum, Bacillus cereus, Enterobacter s., Pseudomonas aeruginosa*	Agar disk diffusion method	172
Glycerol-plasticized cassava starch + pectin + Lemongrass essential oil (LEO)	Lemongrass essential oil (LEO)	*Staphylococcus aureus, Escherichia coli*	Counting method	110
Cassava starch films + Lemongrass essential oil (LEO)	Lemongrass essential oil (LEO)	*Penicillium expansum*	Agar disk diffusion method	175

Starch films + thyme essential oil microcapsules (TEO-M)	Thyme essential oil (TEO)	*Botryodiplodia theobromae Pat.*	Agar disk diffusion method	176
Corn starch (CS) films + clove essential oil (CLEO) + cinnamon essential oil (CEO)	Clove essential oil (CLEO) and cinnamon essential oil (CEO)	*Leuconostoc mesenteroides, Pseudomonas fluorescens, Shewanella putrifaciens*	Agar disk diffusion method	177

Table 5. Mechanical properties of Starch-based EOs films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Cassava starch + processed pumpkin residue extract (PRE) + oregano essential oil (OREO)	**PRE at 3 % and OREO at 0 % concentration:** 1.02 ± 0.06 MPa **PRE at 3 % and OREO at 1 % concentration:** 0.37 ± 0.02 MPa **PRE at 3 % and OREO at 2 % concentration:** 0.39 ± 0.02 MPa	**PRE at 3 % and OREO at 0 % concentration:** 258 ± 5 % **PRE at 3 % and OREO at 1 % concentration:** 236 ± 16 % **PRE at 3 % and OREO at 2 % concentration:** 143 ± 11 %	170
Corn starch films + Orange essential oil (OEO)	**Without OEO:** 5.11 ± 0.57 MPa **With 0.7 µL/g of OEO:** 2.40 ± 0.46 MPa	**Without OEO:** 64.58 ± 8.95 % **With 0.7 µL/g of OEO:** 15.25 ± 2.85 %	168
Starch + oregano (OREO) or thyme (TEO) essential oil	**OREO at 7.5 % concentration:** 0.54 ± 0.03 MPa **OREO at 10 % concentration:** 0.44 ± 0.06 MPa **TEO at 7.5 % concentration:** 0.48 ± 0.05 MPa **TEO at 10 % concentration:** 0.47 ± 0.06 MPa	**OREO at 7.5 % concentration:** 1.06 ± 0.08 % **OREO at 10 % concentration:** 0.92 ± 0.18 % **TEO at 7.5 % concentration:** 1.07 ± 0.05 % **TEO at 10 % concentration:** 0.96 ± 0.11%	169
Starch + Zataria multiflora Boiss (ZEO) or Mentha pulegium (MEO)	**ZEO at 1 % concentration:** Around 13.5 MPa **ZEO at 3 % concentration:** Around 9 MPa **MEO at 1 % concentration:** Around 9 MPa **MEO at 3 % concentration:** Around 3.5 MPa	**ZEO at 1 % concentration:** Around 50 % **ZEO at 3 % concentration:** Around 165 % **MEO at 1 % concentration:** Around 40 % **MEO at 3 % concentration:** Around 110 %	173

Cassava starch + cinnamon essential oil (CEO) + sodium bentonite clay nanoparticles	**Films with 1.5% of CEO:** 0.34 ± 0.02 MPa **Films with 1.5% of CEO and sodium bentonite clay nanoparticles:** 0.63 ± 0.09 MPa **Films with 2% of CEO:** 0.38 ± 0.04 MPa **Films with 2% of CEO and sodium bentonite clay nanoparticles:** 0.54 ± 0.02 MPa	**Films with 1.5% of CEO:** 248.34 ± 26.93 % **Films with 1.5% of CEO and sodium bentonite clay nanoparticles:** 108.85 ± 7.29 % **Films with 2% of CEO:** 270.82 ± 37.05 % **Films with 2% of CEO and sodium bentonite clay nanoparticles:** 96.62 ± 16.56 %	174
Cassava starch + PBAT + oregano essential oil (OREO) encapsulated or free	**Films with free OREO:** 4.5 MPa **Films with OREO encapsulated:** 3.3 MPa	**Films with free OREO:** 10 % **Films with OREO encapsulated:** 9 %	171
Starch films + clove essential oils (CLEO)	**Without CLEO:** 10.52 ± 0.05 MPa **CLEO at 1 % concentration:** 8.60 ± 0.08 MPa **CLEO at 2 % concentration:** 7.16 ± 0.05 MPa **CLEO at 3 % concentration:** 6.25 ± 0.03 MPa	**Without CLEO:** 9.3 ± 0.05 % **CLEO at 1 % concentration:** 7.43 ± 0.01 % **CLEO at 2 % concentration:** 6.25 ± 0.05% **CLEO at 3 % concentration:** 5.67 ± 0.08 %	172
Glycerol-plasticized cassava starch + pectin + Lemongrass essential oil (LEO)	**Without pectin or LEO:** 21 ± 2 MPa **Pectin at 1 wt. % and 0.5 wt % of LEO:** 24 ± 1 MPa **Pectin at 2 wt. % and 1 wt % of LEO:** 16 ± 4 MPa	**Without pectin or LEO:** 2.4 ± 0.2 % **Pectin at 1 wt. % and 0.5 wt % of LEO:** 2.8 ± 0.1 % **Pectin at 2 wt. % and 1 wt % of LEO:** 3.0 ± 0.3 %	110
Cassava starch films + Lemongrass essential oil (LEO)	**Without LEO:** Around 0.65 MPa **4 wt% of LEO:** Around 0.4 MPa		175
Starch films + thyme essential oil microcapsules (TEO-M)	**Film without TEO-M:** 2.1 ± 0.04 MPa **Film with 0.15 g of TEO-M:** 2.3 ± 0.04 MPa **Film with 0.30 g of TEO-M:** 3.1 ± 0.03 MPa **Film with 0.45 g of TEO-M:** 3.4 ± 0.06 MPa	**Film without TEO-M:** 56.8 ± 0.75 % **Film with 0.15 g of TEO-M:** 40.9 ± 0.87 % **Film with 0.30 g of TEO-M:** 30.6 ± 0.51 % **Film with 0.45 g of TEO-M:** 23.5 ± 0.48 %	176

3.3. Chitosan-based Essential Oil Materials

Chitin is considered as the second most abundant natural polymer found in Nature, the first being cellulose[30]. Chitin is a polysaccharide (homopolymer of 2-acetamido-2-deoxy-D-glucopyranose), which is naturally present and extracted in quantity from many invertebrate animals such insects and marine crustaceans (the crab and shrimp, diatom spikes, mollusks), fungi and yeasts (Figure 6). The 50% deacetylation of chitin by alkaline hydrolysis leads to chitosan which is soluble in dilute acids. Chitosan is actually the preferred form of chitin as it is more processable in solution than chitin. This versatile biopolymer has received great attention from researchers due to its versatility like biocompatibility, antimicrobial, antioxidant, and lipid-lowering effects. Interestingly, chitosan is readily converted to films, fibers, beads, powders and coatings and many reviews have described the usefulness of chitosan in paper production, textile finishes, cements, heavy metal chelation, wastewater treatment, fiber and film formations and in biomedical applications.

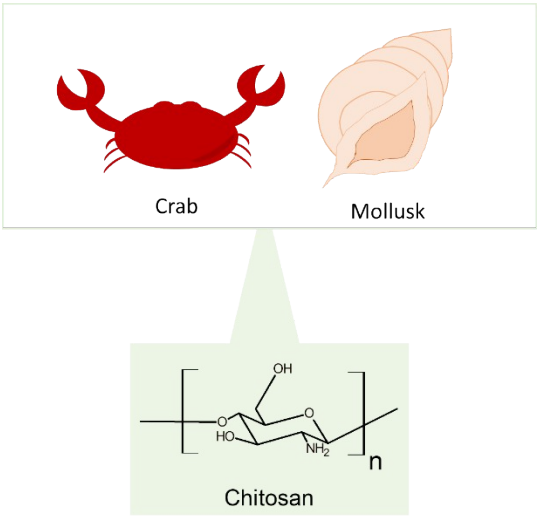

Figure 6. Natural chitosan resources.

Interestingly, the antibacterial activities of solutions of chitosan against both Gram-negative and Gram-positive bacteria depend on a multitude of environmental and structural conditions such as pH, combination with other components, nature of bacteria strains, degree of deacetylation, molecular weight, and concentration [190]. Young et al. highlighted that electrostatic charge interactions between quaternary ammonium groups of chitosan and negatively charged cell membranes are responsible for the leakage of cell membrane and the inhibition of DNA transcription [191-192]. In light of these considerations, pure chitosan films have demonstrated antimicrobial activity against *L. monocytogenes* and *E. coli* [193]. Surprisingly, no antibacterial activities against a series of gram-positive bacteria strains have been observed in native chitosan films in disc diffusion test method [133, 194-196]: this is likely due to the slow diffusion of chitosan through the media, so that only bacteria in direct contact with quaternary ammonium groups of chitosan are inhibited [197]. Interestingly, films made with chitosan and enriched with essential oils have been judged as a promising candidate for the synthesis of innovative antimicrobial materials, however, as previously described, all the mechanisms of antibacterial actions of EOs are not fully understood.

3.3.1. Cinnamon Essential Oil (CEO)

The antibacterial properties of some chitosan-based materials containing cinnamon essential oil (CEO) have been summarized in Table 6. CEO was demonstrated to be one of the more efficient antibacterial compound against *S. aureus* and albeit to a lesser extent against *E. coli*[194]. The minimum inhibitory concentration of CEO for observing *in vitro* antimicrobial effects was around 5 wt% in chitosan films. When 10% of CEO is incorporated in chitosan films, the inhibitory effect of the chitosan-based CEO films has been observed over 3 days (maximum value) and significantly drops after 9 days as the residual CEO concentration inside the films gradually decreases. The inhibition zone reached around 5 cm^2 and 2.25 cm^2 for *S. aureus* and *E. coli* respectively after 3 days. Note that the inhibition time of such hybrid films is likely related to the diffusion of CEO within the polymer matrix, the type and the molecular weight of polymers constituting the films[198-199]. Results are similar to that Hoseini et al.[121] observed against a series of gram-positive bacteria (*L. monocytogenes*, *L. plantarum*, *L. sakei*) and two gram-negative bacteria (*Ps. Fluorescens* and *E. coli*), the antibacterial activity (inhibitory zone) as a function of CEO concentration (v/v) in chitosan film solution (0.4, 0.8, 1.5 and 2%). Not surprisingly, the highest concentration of CEO leads to the highest antibacterial effect (and the largest inhibiratory zone) due to the release of the active component of CEO *i.e.* cinnamaldehyde. Interestingly, the addition of β-cyclodextrin into chitosan-based CEO formulations increases the antimicrobial activities against four types of bacteria strains (*E. coli*, *S. aureus*, *L. monocytogenes* and *S. typhimurium*) in comparison with free CEO. Additionnally, the MIC values for CEO alone is significantly higher than that of β-cyclodextrin/CEO system. Indeed, Sun et al.[118] explained that β-cyclodextrin/CEO may favor water solubility, thus leading to a better contact between CEO and microorganisms, and improving EO antibacterial activity at lower concentrations[200]. Therefore, their results demonstrated that the log reductions for β-CD/CEO in chitosan films (with 1% CEO) reduce respectively the number of *E. coli* and *S. aureus* up to 2.1 and 2.5 logs. Remarkably, this phenomenon is amplified in chitosan/gelatin films when fillers (CEO and rutin) were added[120]. Interestingly, the CEO-based films entirely prevented the *E. coli* growth and led to a 6.5 logs reduction of *L. monocytogenes* after 12h of incubation. This inhibition time is reduced (to 9h) when CEO is combined together with rutin, e.g. a citrus flavonoid glycoside, highlighting thus a synergistic effect of the antibacterial activity. In the meantime, the mechanical strength of the composite films have been improved (Table 7): both TS and the elastic modulus increased whereas the elongation at break (EB) slightly decreased, confirming the intermolecular interactions between CEO and polymer chains. The main components of CEO (*i.e.* trans-cinnamaldehyde, eugenol) interact with the polymer matrix, cause some rearrangement in the polymer chains network, thus strengthening it and increasing the film resistance to elongation [201-203]. As previously mentioned[204], a strong interaction between chitosan polymer chains and CEO induce a cross-linker effect, decreasing thus the free volume and the molecular mobility of the polymer chains. Arrangement of stacking layers of cinnamon essential oil (sheet-like structure) inside the films increases continuities within chitosan network leading to the decrease of EB.

Table 6. Antibacterial properties of chitosan-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Chitosan + cinnamon essential oil (CEO)	Cinnamon essential oil (CEO)	*Escherichia coli* *Staphylococcus aureus* *Aspergillus oryzae* *Penicillium digitatum*	Agar disk diffusion method	194
Chitosan + cinnamon essential oil (CEO)	Cinnamon essential oil (CEO)	*L. monocytogenes* *L. plantarum* *L. sakei* *Ps. Fluorescens* *E. coli*	Agar disk diffusion method	121
Chitosan + cinnamon essential oil (CEO) + β-cyclodextrin	Cinnamon essential oil (CEO)	*E. coli* *S. aureus* *L. monocytogenes* *S. typhimurium*	Counting method	118
Chitosan + gelatin + cinnamon essential oil (CEO)	Cinnamon essential oil (CEO)	*E. coli* *L. monocytogenes*	Counting method	120

Table 7. Mechanical properties of chitosan-based CEOs films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Chitosan + cinnamon essential oil (CEO)	**Chitosan** 5.5 ± 0.6 MPa **Chitosan + CEO** 3.0 ± 0.3 MPa	-	194
Chitosan + cinnamon essential oil (CEO)	**Without CEO:** 10.97 ± 0.5 MPa **CEO at 0.4 %:** 13.35 ± 1.23 MPa **CEO at 2 %:** 29.23 ± 2.25 MPa	**Without CEO:** 24.73 ± 1.86 % **CEO at 0.4 %:** 16.57 ± 0.77 % **CEO at 2 %:** 3.58 ± 0.35 %	121
Chitosan + cinnamon essential oil (CEO) + β-cyclodextrin	**Without CEO:** Around 17 MPa **β-cyclodextrin/CEO at 0.25 %:** Around 17.5 MPa **β-cyclodextrin/CEO at 1 % :** Around 15 MPa	**Without CEO:** Around 31% **β-cyclodextrin/CEO at 0.25 %:** Around 20 % **β-cyclodextrin/CEO at 1 %:** Around 15 %	118
Chitosan + gelatin + cinnamon essential oil (CEO)	**Films without CEO:** 57.6 ± 4.4 MPa **Films with CEO :** 62.2 ± 3.9 MPa	**Films without CEO:** 6.5 ± 1.0 % **Films with CEO :** 4.7 ± 0.7 %	120

3.3.2. Clove Essential Oil (CLEO)

The use of carvacrol as active component of clove essential oil, is also well documented and emerged as an interesting antibacterial compound against a broad range of gram-positive and negative bacteria, fungi, moulds and yeasts[205-206] (Table 8). However, the carvacrol introduction into the water-based chitosan film shows several drawbacks because of its high hydrophobicity and volatility during film casting and drying. To address these issues, arabic gums or glycerol was added into chitosan film formulations to improve carvacrol retention[205] and the addition of cyclodextrins proved their effectiveness for improving compatibility between carvacrol and chitosan polymer chains [207]. Furthermore, it should be underlined that the release rate of the carvacrol from the chitosan based films also depends on chitosan Mw used for film synthesis, being in all cases faster when higher Mw of chitosan is employed during the film synthesis process[208]. In light of these considerations, Fernandez-Pan et al. developed effective antimicrobial chitosan-based films incorporating carvacrol dispersion droplets against three gram-negative strains *i.e. Pseudomona fragi*, *Shewanella putrefaciens* and *Aeromonas hydrophila,* by direct contact. Although *Pseudomona fragi* appears as the most resistant bacteria strain, the increase of Mw of chitosan impacted the growth of these three types of bacteria. Once chitosan-based films were inoculated with bacteria, the hydratation of the corresponding films and the high mobility of the chitosan polymer chains lead to a high rate of carvacrol diffusion in the medium. The hydrophobic carvacrol is accumulated into the cytoplasmic membrane of bacteria, favoring thus interactions with fatty acids and destabilization of the membrane [209]. Interesting antibacterial results were also observed against *S. aureus* and *E. coli*. According to Higueras's investigation it is possible to enhance the loading of hydrophobic carvacrol into hydrophilic chitosan-based film formulations with the addition of a water-soluble cyclodextrin (hydroxypropyl-β-cyclodextrins) and by controlling relative humidity [133]. Antimicrobial activities were observed after 20 days against *S. aureus* and *E. coli*. As expected, the inhibition zone decreases over time while the concentration of carvacrol into films is decreasing: a total inhibition of the bacteria growth is observed for the first 48h (90 mm = inhibition zone); after 8 days of storage, 93% of the initial amount of carvacrol has diffused out of the films and the inhibition zone drops to around 65 mm for both strains and reaches 56 mm after 20 days. Results are in accordance with Sun's study[118] which demonstrated that 1% of carvacrol in chitosan-loaded cyclodextrin film formulations is responsible for the reduction of respectively *E. coli* and *S. aureus* colony forming units (CFUs) by 2.24 and 2.78 logs, and by 1.82 and 1.30 log for *S. typhimurium* and *L. monocytogenes*, respectively. Interestingly, chitosan films incorporated *Thymus piperella* EOs[122] which predominant compound is carvacrol (31.92%), have revealed excellent antibacterial and antioxidant activities against *Serratia marcenscens* (gram-negative), *Aeromonas hydrophila* (gram-negative), *Alcaligenes faecalis* (gram-negative), *Achromobacter denitrificans* (gram-negative) and *Listeria innocua* (gram-positive) for food preservation applications. The same trend was observed with the addition of oregano and thyme essential oils which predominately contain carvacrol[204]. Concerning mechanical properties, the addition of CLEO leads to a loss of TS which is due to the breakup of the chitosan network. Also, the incorporation of CLEO increases the elongation at break, leading to more elastic and extensible films (Table 9).

Table 8. Antibacterial properties of chitosan-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Chitosan films with carvacrol	Carvacrol	*Bacillus subtilis, Escherichia coli, Listeria innocua, Salmonella enteritidis*	Counting method	205
Chitosan films with carvacrol dispersion droplets	Carvacrol	*Pseudomona fragi Shewanella putrefaciens Aeromonas hydrophila*	Agar disk diffusion method	208
Carvacrol-loaded chitosan nanoparticles	Carvacrol	*Staphylococcus aureus Bacillus cereus Escherichia coli*	Counting method (dilution method)	209
Chitosan with hydroxypropyl-β-cyclodextrins and glycerol films	Carvacrol	*Staphylococcus aureus Escherichia coli*	Agar disk diffusion method	133

Chitosan films with Thymus moroderi and Thymus piperella	Thymus moroderi and Thymus piperella	*Serratia marcenscens* *Aeromonas hydrophila* *Alcaligenes faecalis* *Achromobacter denitrificans* *Listeria innocua*	Agar disk diffusion method	122
Chitosan-based films with thyme, clove and cinnamon essential oils	Thyme oil, clove oil and cinnamon essential oil	*Staphylococcus aureus* *Listeria monocytogenes* *Salmonella enteritidis* *Ps. aeroginosa*	Agar disk diffusion method	204

Table 9. Mechanical properties of chitosan-based films containing clove essential oils

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Chitosan-based films with clove essential oil (CLEO)	**Reference without CLEO** 12.20 MPa **Films with 0.5% of CLEO:** 7.855 MPa **Films with 1% of CLEO:** 7.621 MPa **Films with 1.5% of CLEO:** 6.537 MPa	**Reference without CLEO** 25.31 % **Films with 0.5% CLEO:** 41.38 % **Films with 1% of CLEO :** 42.70 % **Films with 1.5% of CLEO :** 37.74 %	204

3.3.3. Thyme and Oregano Essential Oils

Interestingly, chitosan films incorporated thyme essential oils showed higher antibacterial activities against two Gram-positive strains (*Listeria monocytogenes* and *Staphylococcus aureus*) and two Gram-negative strains (*Salmonella enteritidis* and *Ps. Aeroginosa*) than that observed with CEO, and the increase concentration of thyme oil amplifies this phenomenon (Table 10). The release of CEO (and particularly cinnamaldehyde) from chitosan-based films is hindered by chemical interactions with functional groups of chitosan, thus allowing the growth of microorganism surrounding the film during agar diffusion assay. However, Gram-positive bacteria remain more sensitive to carvacrol antibacterial effect than that of Gram-negative ones. For instance, at thyme oil concentration of 1.5 %, the inhibitory zone for *Listeria monocytogenes*, *Staphylococcus aureus, Salmonella enteritidis* and *Ps. Aeroginosa* were 220.13, 162.89, 75.61 and 35.19 mm^2, respectively[204]. Indeed, to explain such a phenomenon, authors argued that cell wall of Gram-negative bacteria is much more complex than Gram-positive ones : besides the presence of peptidoglycan, it contains various polysaccharides, and a multitude of proteins and lipids [210]. The results from Zivanovic et al.[211] seem at odds with previous results as chitosan films enriched with *Origanum vulgare* L. oil lead to 4 logs reduction of *L. monocytogenes* (Gram-positive) and *E. coli* O157:H7 (Gram-negative) in prevention of food pathogens on processed meat. Although the main active component of *Origanum vulgare* L. oil is carvacrol (30.73%) [212], synergistic interactions with thymol and *p*-Cymene may enhance antimicrobial activities against Gram-negative bacteria. In the same way, Zivanovic et al. [211] reported that chitosan-based oregano EO (1 and 2 %) films led to 3.6–4 log. reduction of *L. monocytogenes* growth whereas pure chitosan films displayed only 2 log reduction. Interestingly, the mechanical properties (tensile strength and elongation at break) (Table 11) follow the same trend that was previously observed with the addition of CEO in chitosan films.

Table 10. Antibacterial properties of chitosan-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Chitosan-based films with thyme, clove and cinnamon essential oils	Thyme oil, clove oil and cinnamon essential oil	*Staphylococcus aureus* *Listeria monocytogenes* *Salmonella enteritidis* *Ps. aeroginosa*	Agar disk diffusion method	204
Chitosan films with anise, basil, coriander, and oregano essential oils	Anise oil, basil oil, coriander oil, and oregano oil	*Listeria monocytogenes* *Escherichia coli*	Agar disk diffusion method	211

Table 11. Mechanical properties of chitosan-based EOs films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Chitosan-based films with thyme essential oil (TEO)	**Reference without** TEO 12.20 MPa **Films with 0.5 % of** TEO: 7.182 MPa **Films with 1% of** TEO: 6.897 MPa **Films with 1.5% of** TEO: 5.559 MPa	**Reference without** TEO 25.31 % **Films with 0.5% of** TEO: 35.40 % **Films with 1% of** TEO: 34.62 % **Films with 1.5% of** TEO: 29.86 %	204
Chitosan films with oregano essential oil (OREO)	**Chitosan**: 105.7 N/mm^2 **Chitosan + 1% OREO:** 30 N/mm^2 **Chitosan + 2% OREO**: 18 N/mm^2	**Chitosan**: 5 % **Chitosan + 1% OREO:** 30 % **Chitosan + 2% OREO**: 14 %	211

3.3.4. Bergamot (BEO), ginger (GEO), lemongrass (LEO), and caraway (CAEO) Essential Oils

Other essential oils such as bergamot, lemon, caraway, *Eucalyptus globulus*, tea tree, lemon, rosemary, apricot (*Prunus armeniaca*) kernel essential oils were also employed for antibacterial applications from chitosan-based films (Table 12).

Particularly, the main active antibacterial component of bergamot (BEO), ginger (GEO), lemon (LEO), and caraway (CAEO) essential oils is limonene. For instance, L. Sánchez-González et al.[193] have demonstrated a long-lasting antimicrobial effect up to 12 days against *P. italicum* (CECT 2294) with chitosan-based BO films. From 0 to 5 days of storage, the composite films containing chitosan (CH) with the highest BEO content (3:1, BEO:CH ratio) exhibited the strongest antibacterial inhibition in comparison with native chitosan films. After 5 days of storage, the inhibition properties of BO/chitosan films strongly decreases as the availability and the concentration of BO throughout time drop down. After 12 days, a reduction of more than 2 log units as compared with the native chitosan film is observed. Surprisingly, a different trend was observed by González-Martínez et al with chitosan-based BO and LO films against *Escherichia coli*, *Listeria monocytogenes* and *Staphylococcus aureus* [213]. In this study, CH films without EOs show higher bactericide effects than CH-based EOs. The authors suggested that a strong interaction between the active components of EOs and charged polymer chains limits their diffusion, being thus less available for leading bacterial death. Despite the addition of high concentration of BEO and LEO in chitosan films (3:1 BO (or LO): CH ratio), a slight antimicrobial effect against *L. monocytogenes* is observed, as previously described by Zivanivic et al.[211]. In the same way, the *S. aureus* growth is inhibited when the concentration of BEO and LEO increases. Finally, this trend is only observed for the Gram-positive bacteria (*L.monocytogenes* and *S.aureus*) as CH is less

effective against these microorganisms than that BEO and LEO. The authors concluded that the antimicrobial effect of EOs is amplified when the polymer matrix did not show any antibacterial activity and the EO: polymer ratio increases. Chitosan-based GEO films[214] were also tested as antibacterial agent on pork slices: Wang et al. demonstrated that these films were able to delay the microbial growth on pork by 2.5 logs compared to unwrapped control after 9 days of storage when 1% of EOs is incorporated, suggesting their uses as packaging for meat products. Similar results were obtained with chitosan-based GEO films for extending the shelflife of fish fillets[215]. Interestingly, the addition of GEO nanoemulsions into chitosan-based films strongly decreases by 2 logs factor the total viable counts of microorganisms. Unfortunately, the addition of caraway essential oils (1% volume concentration) in chitosan films has no influence on the antibacterial properties even after 24h of contact with *Escherichia coli* and *Staphylococcus aureus* solutions[216].

Interestingly, the mechanical properties behave differently according to the nature of the introduced EOs (Table 13). For instance, the tensile strength (TS) decreases more than 50% and the percentage of elongation at break (EB) is dramatically reduced by 80% when BEO oils is used, in comparison with the pure chitosan films. The incorporation of the BEO oils leads to less resistant to break and less stretchable materials. The incorporation of BEO oils leads to discontinuities in the chitosan network and changes in the polymer chain interactions resulting in a weak mechanical response[193]. Contrary to the previous results, the addition of caraway EOs within the chitosan matrix decreases slightly TS of the films but remarkably increases EB, probably due to the plasticizing effect of caraway essential oil[217]. Such a trend is also observed with the addition of GEO. Yaru Wang and co-workers explained that GEO oil droplets increased the spatial distance between chitosan polymer chains, also formed a weaker oil-polymer interactions leading to a decrease of TS. The authors also demonstrated that a plastic effect of GEO emulsion was closely linked to its particle size : the smaller the size, the higher the EB. This contributes to a better ductility and resistance ability of chitosan-based materials.

Table 12. Antibacterial properties of chitosan-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Chitosan films with bergamot oil (BEO)	Bergamot oil (BEO)	*Penicillium italicum*	Counting method (dilution method)	193
Chitosan films with bergamot (BEO), lemon (LEO) and tea tree (TTEO) with hydroxypropylmethylcellulose (HPMC)	Bergamot (BEO), lemon (LEO) and tea tree (TTEO)	*Escherichia coli, Listeria monocytogenes, Staphylococcus aureus*	Counting method (dilution method)	213
Chitosan films with mixed cinnamon and ginger oils (ratio of 1:1)	Cinnamon (CEO) and ginger (GEO) oils	*Total microbes on Pork slices*	Counting method (dilution method)	214
Chitosan films with beewax and caraway essential oil	Caraway oil (CAEO)	*Escherichia coli, Staphylococcus aureus*	Counting method (dilution method)	216

Table 13. Mechanical properties of chitosan-based EOs films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Chitosan films with ginger essential oil (GEO)	**Films without GEO:** 19.16 ± 1.55 MPa **Films with 0.5% of GEO coarse emulsion :** 17.78 ± 1.48 MPa **Films with 1% of GEO coarse emulsion:** 13.21 ± 1.42 MPa	**Films without GEO:** 74.55 ± 4.25 % **Films with 0.5% of GEO coarse emulsion:** 85.76 ± 2.94 **Films with 1% of GEO coarse emulsion:** 83.05 ± 3.97 %	215
Chitosan films mixed with bergamot essential oil (BEO)	**Films without BEO:** 113 ± 20 MPa **Films with 0.5% of BEO :** 65 ± 10 MPa **Films with 1% of BEO:** 63 ± 21 MPa **Films with 2% of BEO:** 50 ± 8 MPa **Films with 3% of BEO:** 22 ± 8 MPa	**Films without BEO:** 22 ± 5 % **Films with 0.5% of BEO:** 7 ± 4 % **Films with 1% of BEO:** 5.5 ± 0.7 % **Films with 2% of BEO:** 6 ± 2 % **Films with 3% of BEO:** 1.7 ± 0.4 %	193
Chitosan films with caraway essential oil (CAEO)	**Films without CAEO:** 52.77 ± 0.16 MPa **Films with 1% of CAEO:** 44.47 ± 4.40 MPa	**Films without CAEO:** 14.32 ± 1.33 % **Films with 1% of CAEO:** 31.53 ± 4.28 %	216

3.3.5. Rosemary (REO) and *Eucalyptus globulus* (EGEO) essential oils

Regarding their protective outer membrane, gram-negative bacteria strains remain more resistant to antibacterial molecules than the gram-positive ones against essential oils. However, rosemary (REO) and *Eucalyptus globulus* (EG) essential oils appear as an interesting alternative (Table 14). The high antimicrobial properties of REO are likely due to the presence of phenol diterpenes, such as a-pinene, carnosic acid, carnosol, 1,8-Cineole, rosmanol, isorosmanol, and rosmarinic acid [218-220]. As expected, M. Abdollahi et al. did not show any antibacterial properties of neat chitosan neither in solution nor in films [221-222]: only microorganisms in direct contact with chitosan are inhibited. The addition of 1.5% REO in film-forming solution and disks exert a slight inhibition of *Listeria monocytogenes* (Persian Type Culture Collection 1163), *Streptococcus agalactiae* (PTCC 1768) and *Escherichia coli* (PTCC 1533) growth using agar diffusion method. The authors suggested that the phenolic compounds from REO are mainly responsible for the lipid degradation of cell walls thus leading to the bacterial death. These results are in agreement with those reported by Ponce et al. [220]. Indeed, chitosan film-solutions containing 1% of REO showed limited antimicrobial effects against *L. monocytogenes* thus ruling out any synergic effects of chitosan polymer chains and REO. Interactions between REO and amino group of chitosan may be due to this slight antibacterial effect. However, the addition of REO leads to a softer and more flexible film than that observed with neat chitosan film (Table 15). Interestingly, the tensile strength (TS) and the elongation at break (EB) increase about 7% and 40%, respectively, with the REO %. Authors explain that the increase of TS is due to some interactions in polymer chain as demonstrated by FTIR, and the presence of a cracked structure. The improvement of the percentage of EB results from the increase in moisture content (thanks to REO %) which is well-known as a good plastisizer[222].

The *in vitro* antimicrobial effects of *Eucalyptus globulus* essential oils (EGEO, 4% in volume) introduced in chitosan films is similar to that obtained with REO [195]. The inhibition rate of Gram-negative bacteria (*E. coli, P. aeruginosa*) is higher than that observed with Gram-positive microorganisms (*S. aureus, C albicans*). The inhibitory zone varies from 153.37 mm^2, 118.29 mm^2, 61.35 mm^2 to 98.86 mm^2 for *E. coli, P. aeruginosa, S. aureus* and *C albicans*, respectively. These results are in accordance with those shown by other studies on the antibacterial properties of EGEO[223] which are likely due to the mixture of monoterpenes and oxygenated monoterpenes such as 1,8-Cineole, *p*-Cymene, sphathulenol, eudesmol, thymol, 4-terpinenol, *γ*-Terpinene, 1,8-Menthadien-4-ol, 13-Epimanool and carvacrol[224]. Ojagh et al. have even demonstrated that the incorporation of 1.5% v/v of EGEO in chitosan films reduced by 4.22 logs, 3.98 logs, 4.55 logs and 4.71 logs the growth of *E. coli*, *S. enteritidis, B. cereus* and *S. aureus*, respectively. EGEO not only provide effective antimicrobial properties but also modify mechanical properties of films : indeed, the reduction of TS when rising the % content of EGEO is related to a decrease of intermolecular forces into chitosan films, thus improving their flexibility as previously reported [121].

Table 14. Antibacterial properties of chitosan-based REOs and EGEO films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Chitosan films with rosemary essential oil (REO)	Rosemary essential oil (REO)	*Listeria monocytogenes, Pseudomonas Putida, Streptococcus agalactiae, Escherichia coli, Lactococcus lactis*	Agar disk diffusion method	222
Chitosan films with montmorillonite (MMT) nanoclay and rosemary essential oil (REO)	Rosemary essential oil (REO)	*Listeria monocytogenes, Pseudomonas Putida, Streptococcus agalactiae, Escherichia coli, Lactococcus lactis*	Agar disk diffusion method	221
Chitosan films with oleoresins (olive, rosemary, onion, capsicum, cranberry, garlic, oreganum and carvacrol)	Olive, rosemary, onion, capsicum, cranberry, garlic, oreganum, carvacrol	*Listeria monocytogenes*	Agar disk diffusion method	220
Chitosan films with *Eucalyptus globulus* essential oil	*Eucalyptus globulus* essential oil (EGEO)	*Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa, Candida albicans, Candida parapsilosis*	Agar disk diffusion method	195

Table 15. Mechanical properties of chitosan-based REOs films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Chitosan films with montmorillonite (MMT) nanoclay and rosemary essential oil (REO)	**Chitosan films + MMT (1%) without REO:** 63.74 ± 3.38 MPa **Chitosan films + MMT (1%) + 1% of REO:** 74.66 ± 2.90 MPa **Chitosan films + MMT (3%) + 1% of REO:** 71.45 ± 3.78 MPa	**Chitosan films + MMT (1%) without REO:** 3.56 ± 0.54 % **Chitosan films + MMT (1%) + 1% of REO:** 3.91 ± 0.74 % **Chitosan films + MMT (3%) + 1% of REO:** 4.31 ± 0.27 %	221
Chitosan films with rosemary essential oil (REO)	**Chitosan alone:** 60.80 ± 8.60 MPa **Chitosan films + 0.5% of REO:** 68.51 ± 12.22 MPa **Chitosan films + 1% of REO:** 68.90 ± 13.68 MPa **Chitosan films + 1.5% of REO:** 65.46 ± 4.63 MPa	**Chitosan alone:** 3.56 ± 0.35 % **Chitosan films + 0.5% of REO:** 4.97 ± 0.68 % **Chitosan films + 1% of REO:** 5.07 ± 0.79 % **Chitosan films + 1.5% of REO:** 4.61 ± 0.81 %	222

3.3.6. Lemongrass Essential Oils (LEO)

Antibacterial properties of chitosan/gelatin based LEO films were compared to hybrid Pectin/gelatin based LGEO films in the presence or not of ZnO nanoparticles[111] (Table 16). Globally, Pectin/gelatin films do not show any relevant antibacterial activities against *Escherichia coli*, *Bacillus subtilis* and *Staphylococcus aureus* contray to chitosan/gelatin films alone: the positive charge of the amino group of chitosan may interacts with the negatively charged bacteria membrane, thus provoking leakage of essential constituents of bacteria. For all tested bacteria, the introduction of LEO leads to the slight increase of the diameter of growth inhibition zone. This is likely due to the diffusion of neral, geranial or myrcene which are the major active antibacterial compounds of LEO. Surprisingly, metal oxide nanoparticles did not highly influence the antibacterial properties of these films whatever the nature of the polymer used. There does not appear to have been any synergistic interactions between LEO and ZnO. However, and as expected, the addition of ZnO strongly improve the tensile strength and the flexibility of the hybrid films as well as any inclusion of LEO (Table 17).

Table 16. Antibacterial properties of chitosan-based LGEO films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Chitosan-gelatin films with lemongrass essential oil (LEO)	Lemongrass essential oil (LEO)	*Escherichia coli, Bacillus subtilis, Staphylococcus aureus*	Agar disk diffusion method	111

Table 17. Mechanical properties of chitosan-based LGEO films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Chitosan-gelatin films with lemongrass essential oil (LEO)	**Chitosan-gelatin films** 46.64 ± 1.19 MPa **Chitosan-gelatin films with LEO** 43.51 ± 0.32 MPa **Chitosan-gelatin films with LEO and ZnO:** 50.60 ± 1.33 MPa	**Chitosan-gelatin films** 65.15 ± 2.10 % **Chitosan-gelatin films with LEO** 84.78 ± 2.05 % **Chitosan-gelatin films with LEO and ZnO:** 73.91 ± 6.65 %	111

3.3.7. Tea tree (TTEO) Essential Oils

Antibacterial investigations concerning chitosan-based EOs films are displayed in Table 18. Surprisingly, the use of tea tree (TTEO) essential oils according to González-Martínez et al. investigations[213, 225] seems to have a slight effect on the growth of *E. coli* even with high percentage content. Chitosan may bind with terpens which are the main components of TTO, avoiding their release from the hybrid chitosan films. The authors described a scarce availability of TTEO at the surface of these films. Therefore, it could be concluded that intermolecular interactions which exist between TTEO and chitosan drastically reduce antibacterial effect. The same antibacterial trend is observed with chitosan based TTEO films against *Staphylococcus aureus* and *Listeria monocytogenes.* On the contrary, the replacement of chitosan matrix by hydroxypropylmethylcellulose (which do not present any affinity with chitosan) lead to a tremendous log reduction of *E. coli* and *Listeria monocytogenes* growth (up to 6 log) after 12 days of storage.

Table 18. Antibacterial properties of chitosan-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Chitosan films with bergamot (BEO), lemon (LEO) and tea tree (TTEO) with hydroxypropylmethylcellulose (HPMC)	Bergamot (BEO), lemon (LEO) and tea tree (TTEO)	*Escherichia coli, Listeria monocytogenes, Staphylococcus aureus*	Counting method (dilution method)	213

3.3.8. Orange peel (OPEO) and apricot (*Prunus armeniaca*) kernel (AKEO) Essential Oils

A few studies concern the antibacterial effect of both essential oils in chitosan films (Table 19). Investigations on OPEO-based chitosan films at different concentrations (0, 0.25, 0.5, and 1%) of OPEO against *Staphylococcus aureus* and *Escherichia coli* were done using the agar disk diffusion technique [226]. The higher the concentration of OPEO, the more notable the antimicrobial effect resulting in an enlargement of the inhibitory zone diameter up to reach 30 mm for both pathogens after 24h of incubation. Similar results were obtained with 2% (v/v) OPEO in gelatin films against *S. aureus, B. subtilis, E. coli, P. aeruginosa* and *C. albicans*[227]. However, as the identification of active antibacterial compound is currently unclear, further investigations are of prime importance. Interestingly, the addition of OPEO leads to the decrease of TS which are probably due to structural discontinuities in polymer films induced by OPEO interactions with Gel/CH-based polymer network (Table 20). In contrast, elongation at break (EB) values slightly increased with increasing OPEO %, indicating an increase of film flexibility and stretchability. Surprisingly, opposite mechanical properties are observed with AKEO-based chitosan films[228], i.e. the tensile strength increases and EB decreases when increasing the concentration of AKEO. The polar groups of oleic acid (-OH, -COOH), the main active component of AKEO, establish covalent bonds with amino and hydroxy groups of chitosan polymer chains resulting in constrained motion of the chitosan chains. Concerning the antibacterial properties of chitosan-based AKEO films, few studies[228-229] have been described. For instance, Priyadarshi et al.[228] suggested that the low inhibition effect on the population of *B. subtilis* and *E. coli* was observed after 4h of incubation and presumed that *N*-methyl-2-pyrrolidone (NMP) may dissolve lipids of cell membrane leading to its disintegration and the release of intracellular fluids. On the contrary, chitosan-based AKEO films totally inhibit the growth of *Listeria monocytogenes*[229].

Table 19. Antibacterial properties of chitosan-based OPEO and AKEO films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Chitosan and fish skin gelatin films with orange peel essential oil (OPEO)	Orange peel essential oils (OPEO)	*Staphylococcus aureus, Escherichia coli*	Agar disk diffusion method	226
Chitosan films with orange peel essential oil (OPEO)	Orange peel essential oils (OPEO)	*Staphylococcu aureus, Bacillus subtilis, Escherichia coli, Pseodomonas aeruginosa, Candida albicans*	Agar disk diffusion method	227
Chitosan films with Apricot kernel essential oil (AKEO)	Apricot kernel essential oils (AKEO)	*Bacillus subtilis, Escherichia coli*	Counting method (dilution method)	228
Chitosan films with Apricot kernel essential oil (AKEO)	Apricot kernel essential oils (AKEO)	*Listeria monocytogenes*	Counting method (dilution method)	229

Table 20. Mechanical properties of chitosan-based OPEO and AKEO films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Chitosan and fish skin gelatin films with orange peel essential oils (OPEO)	**Film without OPEO:** 22.53 ± 0.38 MPa **Film with 0.25 % (v/v) of OPEO:** 20.43 ± 0.82 MPa **Film with 0.5 % (v/v) of OPEO:** 19.35 ± 0.31 MPa **Film with 1 % (v/v) of OPEO:** 17.80 ± 0.91 MPa	**Film without OPEO:** 2.52 ± 0.17 % **Film with 0.25 % (v/v) of OPEO:** 2.73 ± 0.04 % **Film with 0.5 % (v/v) of OPEO:** 3.55 ± 0.07 % **Film with 1 % (v/v) of OPEO:** 4.23 ± 0.23 %	226
Chitosan films with Apricot kernel essential oil (AKEO)	**Chitosan films without AKEO:** 9.45 ± 0.53 MPa **Chitosan films with AKEO ratio 1:0.5 (w/v):** 17.67 ± 0.98 MPa **Chitosan films with AKEO ratio 1:1 (w/v):** 19.36 ± 1.06 MPa	**Chitosan films without AKEO:** 4.86 ± 0.63 % **Chitosan films with AKEO ratio 1:0.5 (w/v):** 4.02 ± 0.14 % **Chitosan films with AKEO ratio 1:1 (w/v):** 3.76 ± 0.43 %	228

3.4. Poly(lactic) acid (PLA)

Polylactic acid (PLA) is considered as a prominent thermoplastic biopolymer and promising candidate for many applications due to its

properties, such as its elasticity, rigidity, thermoplastic behavior, biocompatibility, biodegradability, recyclability and non-toxicity [31]. PLA is a linear aliphatic and biocompatible polyester which can be produced using a two-step chemical process [32] (Figure 7): the first step includes the lactic acid production (by chemical synthesis of acetaldehyde or by carbohydrates fermentation process) followed by the ring-opening polymerization (ROP) of LA or lactides in the presence of metal catalysts or by polycondensation. PLA is also biotechnologically synthesized by direct fermentation of metabolically engineered bacteria or by enzymatic catalysis. Globally, the PLA market reached $ 535.6 million in 2019 and is expected to rise up 15.9% in the next ten years. Due to its promissing properties including low environmental impact, biocompatibility, thermal stability, tunable mechanical properties and processability, PLA can replace conventional petro-sourced polymers such as polyethylene, polypropylene, polyethylene terephthalate and polystyrene [230]. Recent PLA applications concern automotive, food packaging industry, thermal insulation, medical field including porous scaffolds for tissue engineering, medical implants, surgical sutures, medical equipment, drug carriers and biomedicine to control infectious diseases. Despite the current demand for the design of innovative materials to provide inhibition of microbial growth and preventing subsequent adhesion and proliferation of microorganisms, the use of PLA-based antimicrobial materials is scarce.

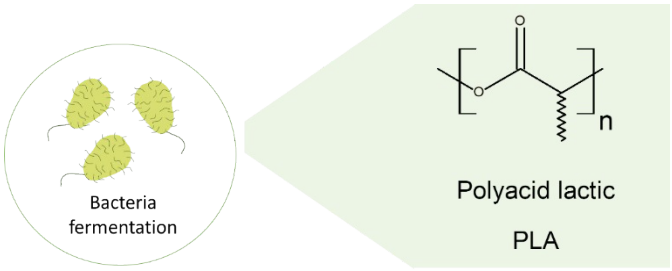

Figure 7. Polylactic acid (PLA).

Few studies used PLA-based EOs as composite antimicrobial films (Table 21). Liu et al. first reported the significant antibacterial effect of PLA/PCL blend/oregano essential oil (OREO) against *E. coli* and *L. monocytogenes* according to the counts of colony-forming units (CFU) [231]. After 24h of incubation, PLA-based OEO films (9 wt% of OEO) lead to 3.5 logs reduction of *L. monocytogenes* and *E. coli.* This strong antimicrobial effect is likely due to the gradual release of OEO over time, and more specifically to the diffusion of carvacrol and thymol (which are the most active phenolic compound of OEO) toward the cell membrane. These results are not surprising as OEO is considered as the most effective antimicrobial essential oils [232-233]. Carvacrol and thymol, are expected to induce functional damages to the bacteria cytoplasmic membrane [234]. Results are in total agreement with those described by Salmieri et al. with poly(lactic acid)–cellulose nanocrystals incorporating OREO which promoted a quasi-total inhibition of *L. monocytogenes* after 14 days of incubation after a slow controlled release of phenolic biactive compounds [235]. Javidi et al. also demonstrated that the inclusion of 0.5 wt% of OREO into PLA matrix slightly inhibit the growth of *S. aureus*, *L. monocytogenes* and *S. enteritidis* without affecting *E. coli* : the outer membrane surrounding gram-negative (*E. coli*) bacteria wall is protected by lipopolysaccharides, thus limiting the diffusion of hydrophobic active substances of OEO to *E. coli* [236]. However, with the increasing concentration of OEO up to 1.5 wt%, the inhibition area is strongly enlarged ranging from 230.5 ± 0.3 mm^2 for *E. coli* to 722.5 ± 0.1 mm^2 for *S. aureus.* Overall, the addition of OREO into PLA matrix caused a significant decrease of the tensile strength (TS) due to a plasticizing effect of OREO and phase separated structures (Table 22). On the contrary, a remarkable increase of elongation at break was observed leading to films with improved flexibility and ductibility [236,231].

Similarly to OEO, *Zataria multiflora Bioss* essential oil (ZME) is a rich source of phenolic terpenes, essentially carvacrol and thymol[237]. Rezaeigolestani et al. have successfully developed antimicrobial PLA composites films with different concentrations of ZME by solvent casting[238]. The antibacterial effects of the corresponding films against *S. aureus*, *E. coli*, *V. parahaemolyticus* and *L. monocytogenes* were evaluated by disk diffusion method. All the tested PLA-based ZME films showed antimicrobial properties which are reinforced in higher ZME concentrations. The addition of ZME also modify the mechanical properties of the PLA composites with an increase of EB and a reduction of TS: ZME facilitates the movement of the adjacent PLA chains improving their flexibility and making stiff polymers[238]. In line with the previous investigations, it was demonstrated that the addition of clove essential oil (CLEO) in PLA/PEG/PCL films acts not only as a plasticizer by permitting chain mobility (a drop of TS to 10.93 MPa and a significant improvement of EB to 204% are observed in comparison with reference without EOs) but also as effective antimicrobial agents[239] : indeed, CEO reduces by 2 and 4 logs the growth of *S. aureus* and *E. coli* after 7 days. The complete inhibition of *E. coli* was observed on the same period after the addition of ZnO nanoparticles. The authors indicate a synergistic effect between eugenol (the main volatile active molecules found in CEO) and ZnO, thus allowing the hydrophobic compounds from CEO and Zn cations to penetrate through the bacterial cell membrane provoking their death. Recently, cinnamomum cassia essential oil (CCEO), eugenol (EEO), and linalool (LEO) have been introduced in PLA capsules according to the emulsion solvent evaporation method[240] (Figure 8). The average size values of the CCEO-PLA, EEO-PLA, and LEO-PLA capsules were evaluated at (80.1 ± 2.6) µm, (23.4 ± 1.6) µm, and (75.2 ± 2.3) µm respectively. Relevant antibacterial acitivities were demonstrated with CCEO-PLA capsules over a period of 28 days against two Gram-negative strains (*E. coli* and *Salmonella*) and two Gram-positive cultures (*S. aureus* and *L. monocytogenes*). *Salmonella* and *L. monocytogenes* seem to be the most sensitive to CCEO. The inhibition zone diameters reach a maximum of 80 mm (after 28 days of incubation) and 90 mm (after 14 days of incubation) for *Salmonella* and *L. monocytogenes* respectively. Although an inhibition zone remains visible in CCEO-PLA based systems, *E. coli* and *S. aureus* appear less sensitive to CCEO. The weak antibacterial activities of EEO-PLA and LEO-PLA capsules against the same strains during 28 days of incubation were explained as low capsule stability over time, to a likely interaction with PLA matrix and a potential low thermal stability. Future challenges will be to encapsulate EOs in other polymeric matrix avoiding potential chemical interactions. Interestingly, Stoleru and coworkers have demonstrated a new concept based on the combination of surface modification and emulsion entrapment method[117].

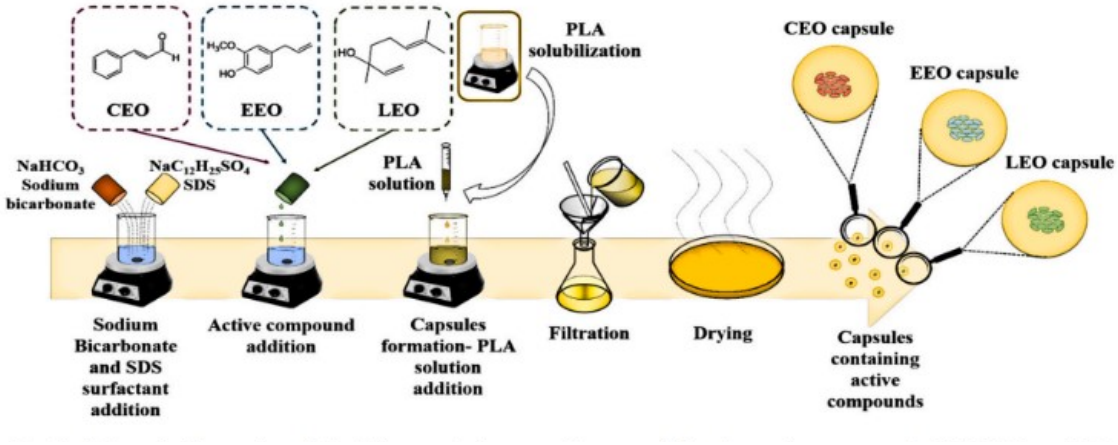

Figure 8. Synthesis of the EOs based PLA capsules according to the emulsion solvent evaporation method. Reprinted with permission from ref [240]. Copyright 2021 Elsevier.

Table 21. Antibacterial properties of PLA-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
PLA/PTMC films with oregano essential oil (OREO)	Oregano essential oil (OREO)	*Listeria monocytogenes, Escherichia coli*	Counting method	231
Supramolecular poly(lactic acid)–cellulose nanocrystals (PLA–CNC) nanocomposite films	Oregano essential oil (OREO)	*Listeria monocytogenes*	Counting method (dilution method)	235
PLA films	Oregano essential oil (OREO)	*Staphylococcus aureus, Listeria monocytogenes, Salmonella enteritidis*	Agar disk diffusion method	236
PLA composite films with propolis ethanolic extract (PEE) and cellulose nanofiber (CNF)	Zataria multiflora Bioss essential oil (ZME)	*Staphylococcus aureus*, *Escherichia coli*, *Vibrio parahaemolyticus, Listeria monocytogenes*	Counting method (dilution method)	238
PLA/PEG/PCL films with zinc oxide (ZnO) and clove essential oil (CLEO)	Clove essential oil (CLEO)	*Staphylococcus aureus, Escherichia coli*	Counting method (dilution method)	239

PLA capsules with cinnamomum cassia essential oil (CCEO), eugenol (EEO), and linalool	Cinnamomum cassia (CCEO), eugenol (EEO), and linalool essential oils	*E. coli, Salmonella, S. aureus, L. monocytogenes*	Agar disk diffusion method	240
PLA films with chitosan and apricot (AKEO) and clove (CLEO) essential oils.	Apricot (AKEO) and clove (CLEO) essential oils.	*Listeria monocytogenes, Salmonella Typhimurium, Escherichia coli*	Counting method (dilution method)	117

Table 22. Mechanical properties of PLA-based EOs films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
PLA/PTMC films with oregano essential oil (OREO)	**PLA/PTMC without OREO:** 12.38 ± 1.15MPa **PLA/PTMC with 3 % wt of OREO:** 13.00 ± 1.32 MPa **PLA/PTMC with 12 % wt of OREO:** 11.29 ± 1.56 MPa	**PLA/PTMC without OREO:** 105.51 ± 29.03 **PLA/PTMC with 3 % wt of OREO:** 177.99 ± 24.17 % **PLA/PTMC with 12 % wt of OREO:** 190.84 ± 13.37 %	231
Supramolecular poly(lactic acid)–cellulose nanocrystals (PLA–CNC) nanocomposite films	**PLA–CNC without OREO at day 0:** 1169 MPa **PLA–CNC without OREO at day 14:** 1349 MPa **PLA–CNC- OREO at day 0:** 343 MPa **PLA–CNC- OREO at day 14:** 550 MPa	**PLA–CNC without OREO at day 0:** 3.2 % **PLA–CNC without OREO at day 14:** 3.0 % **PLA–CNC- OREO at day 0:** 27.2 % **PLA–CNC- OREO at day 14:** 3.2 %	235
PLA films with oregano essential oil (OREO)	**PLA films without OREO:** 47.18 ± 6.01 MPa **PLA films with 1% w/w of OREO :** 18.36 ± 0.75 MPa **PLA films with 1.5% w/w of OREO:** 15.73 ± 1.10 MPa	**PLA films without OREO:** 2.82 ± 0.46 % **PLA films with 1% w/w of OREO:** 15.45 ± 0.98 MPa **PLA films with 1% w/w of OREO:** 14.18 ± 0.77 %	236
PLA composite films with propolis ethanolic extract (PEE) and cellulose nanofiber (CNF)	**PLA/CNF/PEE without ZME:** 20.3 ± 0.29 MPa **PLA/CNF/PEE with 0.5% of ZME:** 16.1 ± 0.17 MPa **PLA/CNF/PEE with 1% of ZME:** 11.6 ± 0.15 MPa	**PLA/CNF/PEE without ZME:** 47.1 ± 2.0 % **PLA/CNF/PEE with 0.5% of ZME:** 69.3 ± 0.6 % **PLA/CNF/PEE with 1% of ZME:** 63.2 ± 2.1 %	238
PLA/PEG/PCL films with zinc oxide (ZnO) and clove essential oil (CLEO)	**PLA/PEG/PCL films:** 13.97 MPa **PLA/PEG/PCL films with CLEO:** 10.93 MPa **PLA/PEG/PCL films with ZnO:** 21.38 MPa **PLA/PEG/PCL films with ZnO and CLEO:** 13.96 MPa	**PLA/PEG/PCL films:** 25.48 % **PLA/PEG/PCL films with CLEO:** 204 % **PLA/PEG/PCL films with ZnO:** 17.72 % **PLA/PEG/PCL films with ZnO and CLEO:** 136.1 %	239

3.5. Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are promising bio-based polymers due to their inherent biocompatibility, biodegradability, and environment-friendly properties[33]. They are thermoplastic bacterial polyesters used as carbon and energy storage, which are produced from numerous microorganisms (Gram-negative and Gram-positive bacteria) when essential nutrient such as oxygen, nitrogen or phosphorus is limiting or after pH strongly shifts[241-244] (Figure 9). Polyesters are accumulated in bacteria cytoplasm as granular inclusions under stress conditions, and when nutrients are limiting, PHAs are degraded allowing bacterial growth. Up to date, around 150 different types of straight, branched, saturated, unsaturated and aromatic PHAs have been reported by over 300 generations of bacteria species [245-246]. Despite the high production costs of PHAs, scientist community focus their attention on developing both new polymer extraction process with reduced costs and much more efficient fermentative pathways[247]. PHAs are structurally classified into two groups : short chain length (*scl*) or medium chain length (*mcl*) polyesters according to the carbon atoms number in the chain of the branching polymers ranging from 3 to 14 carbon atoms[248]. *scl* PHAs consist in 3–5 carbon atoms (poly (3-hydroxybutyrate), poly(4-hydroxybutyrate) and poly(3-hydroxyvalerate)) whereas *mcl* PHAs have 6 to 14 or more than 14 carbon atoms (poly (3-hydroxyhexanoate), poly(3-hydroxyoctanoate) for example[249]. PHAs are potential candidates for a wide range of applications including packaging materials, food additives, pressure sensors, tissue engineering, controlled drug release and medical devices in general[144, 246, 250].

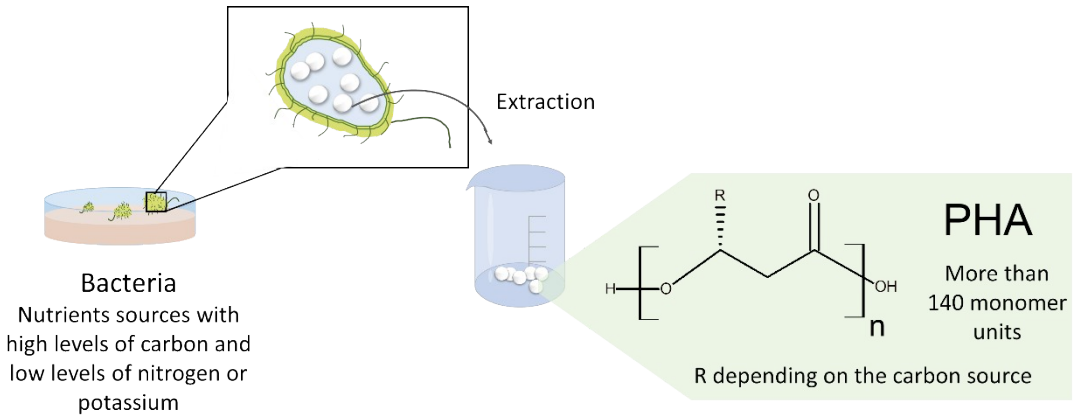

Figure 9. Structure of Polyhydroxyalkanoates (PHAs).

Unfortunately, as PHAs do not show any inherent antibacterial properties, innovative strategies have been developed for tailoring their properties[251-254], or PHAs could be blended with antimicrobial additives such as essential oils[255]. The later strategy is a feasible option for the design of biodegradable antimicrobial materials (Table 23). However, the loss of volatiles EOs during the film production process could be a limiting issue. For instance, and to overcome this problem, Requena et al. obtained poly[(3-hydroxybutyrate)-*co*-(3-hydroxyvalerate)] (PHBV) bilayer films incorporated separately oregano essential oil (OREO), carvacrol (CA), clove essential oil (CLEO) and eugenol (EU) at the interface by thermo-compression technique[135]. The resulting PHA-based EOs exhibited significant antimicrobial activities against *Listeria innocua* and *Escherichia coli*. A total inhibition of *E. coli* growth is observed with PHBV-based OR, CA or EU films as previsouly described[256-258]. Interestingly, and for both bacteria, PHBV-based CLO films seem to be the least effective. The authors suspected a possible crosslinking effect of CLO with PHBV matrix, thus inhibiting its release and therefore decreasing its antimicrobial action against *Listeria innocua* and *Escherichia coli*. To preserve the original antimicrobial properties of EOs, Lagaron et coworkers used electrospinning technique to facilitate the introduction of thermolabile compounds into PHBV-based materials[259]. Therefore OREO, REO and green tea extract (GTE) were introduced in electrospun PHBV fibers and the strongest antimicrobial properties have been demonstrated with OREO against *E. coli* and *S. aureus*. A tremendous inhibition of the *S. aureus* growth with more than 3 logs reduction was observed whereas a slightly lower reduction was demonstrated with *E. coli* (2.7-2.9 logs decrease) after 15 days. These results are amplified when materials are put in closed medium. For REO and GTE, the log reductions remain one or two times lower than that observed with OREO for both strains. The authors ascribed this phenomenon to the release of the active EOs which concentration increase in closed medium. The same group highlighted that the introduction of ZnO NPs in ORE-based electrospun PHBV increases the antibacterial long-term performance of the materials up to 48 days[260-261]. In addition to the biocide effect of OREO, it would seem that the strong antibacterial activities are also due to the release of Zn^{2+} ions and reactive oxygen species causing irreversible damage in the membrane cell wall[262].

All of these results precisely highlighted that the nature of the polymer matrix, its interaction with EOs as well as the film synthesis process greatly influence the antimicrobial properties of the films (Table 24). The addition of EOs also highly modify the mechanical properties of the PHBV-derived materials, but mechanical results seem sometimes contradictory. The incorporation of EOs significantly reduces TS and EAB resulting in a poor stretchability of the PHBV derived materials[135]. On the contrary, the improvement in ductility with the addition of OEO was reported by Figueroa-Lopez et al.[260] and Melendez-Rodriguez et al.[263]. OEO is considered as a plasticizer, reduces the intermolecular forces between oils and PHBV chains along with an increase of their mobility.

Table 23. Antibacterial properties of PHAs-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
PHBV films with oregano essential oil (OREO), carvacrol (CA), clove essential oil (CLEO) and eugenol (EU)	oregano essential oil (OREO), carvacrol (CA), clove essential oil (CLEO) and eugenol (EU)	*Listeria innocua, Escherichia coli*	Counting method (dilution method)	135
PHBV fibers with oregano essential oil (OREO), rosemary extract (RE), and green tea extract (GTE)	Oregano essential oil (OREO), rosemary extract (RE), and green tea extract (GTE)	*Staphylococcus aureus, Escherichia coli*	Counting method (dilution method)	259
PHBV fibers with oregano essential oil (OREO) and zinc oxide nanoparticles (ZnONPs)	Oregano essential oil (OREO)	*Staphylococcus aureus, Escherichia coli*	Counting method (dilution method)	260
PHBV fibers with oregano essential oil (OREO) and zinc oxide nanoparticles (ZnONPs) with/without barrier coatings of cellulose nanocrystals (CNCs)	Oregano essential oil (OREO)	*Staphylococcus aureus, Escherichia coli*	Counting method (dilution method)	261

Table 24. Mechanical properties of PHAs-based EOs films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*

PHBV films with oregano essential oil (OREO), carvacrol (CA), clove essential oil (CLEO) and eugenol (EU)	**PHBV:** 27.6 ± 27.6 MPa **PHBV-OREO:** 17.3 ± 0.6 MPa **PHBV-CA:** 17.6 ± 1.1 MPa **PHBV-CLEO:** 18.2 ± 1.2 MPa **PHBV-EU:** 17 ± 2 MPa	**PHBV:** 5.3 ± 0.4 % **PHBV-OREO:** 3.8 ± 0.4 % **PHBV-CA:** 4.4 ± 0.6 % **PHBV-CLEO:** 3.9 ± 0.4 % **PHBV-EU:** 3.8 ± 0.4 %	135
PHBV fibers with oregano essential oil (OREO) and zinc oxide nanoparticles (ZnO NPs)	**PHBV:** 12.6 ± 2.7 MPa **PHBV + 10 wt% of OREO:** 18.5 ± 0.5 MPa **PHBV + 3 wt% of ZnO NPs:** 17.1 ± 0.9 MPa **PHBV + 2.5 wt% OREO + 2.25 wt% of ZnO NPs:** 14.5 ± 2.4 MPa **PHBV + 5 wt% OREO + 1.5 wt% of ZnO NPs:** 14.8 ± 4.5 MPa **PHBV + 7.5 wt% OREO + 0.75 wt% of ZnO NPs:** 14.1 ± 3.8 MPa	**PHBV:** 1.71 ± 0.35 % **PHBV + 10 wt% of OREO:** 4.53 ± 0.41 % **PHBV + 3 wt% of ZnO NPs:** 1.26 ± 0.23 % **PHBV + 2.5 wt% OREO + 2.25 wt% of ZnO NPs:** 3.28 ± 0.32 % **PHBV + 5 wt% OREO + 1.5 wt% of ZnO NPs:** 4.35 ± 1.28 MPa **PHBV + 7.5 wt% OREO + 0.75 wt% of ZnO NPs:** 5.01 ± 1.34 %	260

3.6. Proteins

Commonly, proteins consist in combination, interaction and adhesion of a multitude of amino acids in various positions[264] which confer to proteins a wide range of functional properties such as high intermolecular binding ability. Proteins have been extensively used for synthesizing biodegradable films or coatings as they provide some advantages such as relative high abundance, excellent gas barrier properties, solubility in water, and satisfactory mechanical properties. They recently gained a great interest in the synthesis of edible films for food packaging.

3.6.1. Gelatin

The hydrolysis of collagen extracted from skin and bones of animals produces gelatin which physical and chemical properties are predominantly affected by collagen type, the age of animal, and the extraction process[265]. With an annual growth rate of 3.73% from 2012 to 2018, and an annual production of 450.7 kilo tons in 2018, gelatin appears as one of the most intensively proteins studied, and its filming properties make gelatin to be used for extending the food products shelf life. To date, gelatin-based films have gained increasing importance and is described as one of the most widely biopolymer used for film processing domain. For instance, many biocide agents have been incorporated into gelatin-based films[266-268] such as metal ions, organic acids, and polymers, to produce performing antibacterial films. In the following section, only investigations dealing with gelatin-based films containing EOs will be described (Table 25).

Hosseini et al. have developed antibacterial bio-based films from fish gelatin and chitosan NPs[267] incorporating *Origanum vulgare L.* essential oil (OREO). OREO demonstrated its effectiveness against two Gram-negative bacteria, *Salmonella enteritidis* and *Escherichia coli*, and both *Staphylococcus aureus* and *Listeria monocytogenes* (Gram-positive bacteria) in a concentration-dependent manner. Although it is well accepted in literature that Gram-positive are slightly more sensitive to EOs than Gram-negative[156], this study tends to show the opposite. A minimum concentration of 1.2% (w/v) of OEO leads to inhibition halos between 30 and 33 mm for *Salmonella enteritidis* and *Escherichia coli* respectively, and 26 mm for both Gram-positive. Authors justified these observations by the fact that carvacrol (the major active component from OEO) shows more affinity towards Gram-negative bacteria than Gram-positive ones[269]. Carvacrol also forms channels in the bacteria membrane by pulling apart the fatty acid chains, leading to the diffusion of ions from the cytoplasm[156]. Another study highlighted the role of CEO into gelatin-based films[270] and are opposite to those described by Hosseini[267]. Gram-positive bacteria (*Staphylococcus aureus*) would be slightly more sensitive to CEO than gram-negative ones (*Escherichia coli*) as they allow diffusion of hydrophobic compounds through its lipopolysaccharide membrane[156]. Nevertheless, the higher the concentration of CEO (up to 6%), the larger the inhibition halos of gelatin-based films. Indeed, CEO reacts with the phospholipid cell membrane of bacteria, increasing thus the permeability and the leakage of their cytoplasm. Interestingly, CEO shows higher inhibition effect on fungi (*Aspergillus niger, Rhizopus oryzae* and *Paecilomyces varioti*) than bacteria. Zhang et al. observed that cinnamaldehyde[271], the main active constituent of CEO, significantly influences the fungal cellular ultrastructure by degrading organelles, and interfering in the synthesis of cell wall and cytoplasm (solidification, degeneration). It is interesting to highlight the long-term antibacterial effect of gelatin-based films incorporating CEO: this is likely due to the

formation of intermolecular hydrogen bonds between amino acid residues of gelatin and aldehyde group of CEO, so that cinnamaldehyde is slowly released from the films. To improve mechanical properties and water vapor permeability of films for food packaging, Cloisite Na^+ is often used[272]. Therefore Saranti et al. have developed new antibacterial gelatin films[273] reinforced with cloisite Na^+ and black pepper EO loaded nanoemulsions. First, the addition of EO nanoemulsion with clay dispersion decreased TS as compared with the control films without EO. Both hydrophobic EO and clay particle, two reinforcing agents, hinder the mobility of the polymer chains. Second, such nanoemulsions improve the inhibition growth of *E. coli* and *S. aureus*.

Recently, Cui et al. successfully highlighted the long-term antibacterial activity[274] of clove oil (CO) introduced into chitosan (CO@CNPs) and loaded into gelatin electrospun nanofibers (gelatin/CO@CNPs). This original system displayed significant inhibition effect against the formation of *E. coli* biofilms. After 24h of incubation, more than 99.7% reduction of *E. coli* population was observed. This trend is likely due to the release of CO which accelerates by increasing temperature after dissolution of gelatin. This new concept was also described by the same team for the fabrication of gelatin-based nanofibers incorporating moringa oil-loaded chitosan NPs to fight against the growth of *Listeria monocytogenes* and *Staphylococcus aureus*[275]. Similarly, Tang et al. described the synthesis of electrospun gelatin nanofibers incorporating peppermint essential oil (POEO) and chamomile essential oil (COEO) for potential antibacterial packaging[276] against *E. coli* and *S. aureus*. Particularly, POEO displays more significant bacterial growth inhibition (3 and 2.5 logs reduction for *E. coli* and *S. aureus* respectively) than that observed with COEO (2 and 1.5 logs reduction for *E. coli* and *S. aureus* respectively). The authors explained such a phenomenon by the presence of menthol, a remarkable active antibacterial compound in POEO[277].

Regarding the mechanical properties (Table 26), the addition of OREO[267] causes a significant decrease of TS due to the presence of structural discontinuities in polymer matrix[225] while a significant increase of EB was observed: the plasticizing role of essential oil introduced in the gelatin matrix resulted in the increase of ductile properties in accordance with Ramos and coworkers[256]. On the contrary, the incorporation of CEO oil droplets in the gelatin films structure makes the film inhomogeneous, promoting weaker bondings between gelatin chains, leading to the breakup of the gelatin network microstructure and the drop of TS and EAB values[270].

Table 25. Antibacterial properties of gelatin-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Fish gelatin and nanoparticules of chitosan with OREO	*Origanum vulgare L.* essential oil (OREO)	*Staphylococcus aureus, Listeria monocytogenes, Salmonella enteritidis, Escherichia coli*	Agar disk diffusion method	267
Fish gelatin films with cinnamon essential oil	Cinnamon essential oil (CEO)	*Escherichia coli, Staphylococcus aureus, Aspergillus niger, Rhizopus oryzae, Paecilomyces varioti*	Agar disk diffusion method	270
Gelatin films with black pepper essential oil-loaded nanoemulsions and Cloisite Na+	Black pepper essential oil	*Escherichia coli, Staphylococcus aureus.*	Agar disk diffusion method	273
Films of chitosan loaded into gelatin electrospun nanofibers (gelatin/CO@CNPs) with cloves oil	Clove essential oils (CLEO)	*Escherichia coli*	Counting method (dilution method)	274

Films with moringa oil-loaded chitosan nanoparticles (MO@CNPs) and embedded gelatin nanofiber	Moringa essential oil	*Listeria monocytogenes, Staphylococcus aureus*	Broth dilution method	275
Electrospun gelatin nanofibers with peppermint essential oil (POEO) and chamomile essential oil (COEO)	Peppermint essential oil (POEO) and chamomile essential oil (COEO)	*Escherichia coli, Staphylococcus aureus*	Optical density with a UV-vis spectrometer	276

Table 26. Mechanical properties of gelatin-based EOs films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Fish gelatin and nanoparticules of chitosan with oregano essential oil (OREO)	**Films without OREO:** 10.57 ± 0.19 MPa **Films with 0.4 % of OREO:** 6.72 ± 0.4 MPa **Films with 0.8 % of OREO:** 5.41 ± 0.78 MPa **Films with 1.2 % of OREO:** 3.28 ± 0.43 MPa	**Films without OREO:** 44.71 ± 11.80 % **Films with 0.4 % of OREO:** 151.82 ± 4.78 % **Films with 0.8 % of OREO:** 104.26 ± 38.28 % **Films with 1.2 % of OREO:** 87.20 ± 17.14 %	267
Fish gelatin films with cinnamon essential oil (CEO)	**Films without CEO:** 29.03 ± 0.92 MPa **Films with 0.5 % of CEO:** 17.77 ± 1.93 MPa **Films with 1 % of CEO:** 12.66 ± 1.47 MPa **Films with 2 % of CEO:** 8.55 ± 0.39 MPa **Films with 6 % of CEO:** 4.64 ± 1.19 MPa	**Films without CEO:** 160.43 ± 5.49 % **Films with 0.5 % of CEO:** 125.60 ± 2.50 % **Films with 1 % of CEO:** 119.05 ± 1.41 % **Films with 2 % of CEO:** 95.55 ± 2.54 % **Films with 6 % of CEO:** 84.33 ± 5.37 %	270
Gelatin films with black pepper essential oil (BPEO)-loaded nanoemulsions and Cloisite Na+	**Films without BPEO:** 57.16 ± 3.54 MPa **Films with BPEO at 12,000 rpm, 2 min:** 64.05 ± 2.61 MPa	**Films without BPEO:** 2.96 ± 0.39 % **Films with BPEO at 12,000 rpm, 2 min:** 7.77 ± 0.91 %	273
Films with moringa oil-loaded chitosan nanoparticles (MO@CNPs) and embedded gelatin nanofiber	**Gelatin films with MO@CNPs at 3.0 mg/mL:** 0.76 ± 0.31 MPa **Gelatin films with MO@CNPs at 15.0 mg/mL:** 1.02 ± 0.33 MPa	**Gelatin films with MO@CNPs at 3.0 mg/mL:** 54.57 ± 1.96 % **Gelatin films with MO@CNPs at 15.0 mg/mL:** 49.47 ± 2.69 %	275

3.6.2. Casein

Casein constitutes the predominant protein in mammalian milk and in dairy products. The excellent functional properties and natural

abundance of casein allow its extensive use in manufactured products in the food industry such as in bakery applications, beverages, milk product, and many studies reported its use for chemical, biological and nutritional applications[278-279]. For instance, the world market of casein or caseinates used in food industry are reported to reach 2,500,000 tons per year[280]. Due to its strong cohesive interactions reflecting high intermolecular hydrogen, electrostatic and hydrophobic bonds, the formation of films in aqueous media without additional processing is highly probable. Many advantages such as biodegradability, non-toxicity, high thermal stability, the capability to form micelles and bind small molecules, make casein an incredible protein to synthesize desirable biodegradable materials for the preparation of edible or food packaging films[279]. Indeed, the distribution of the amino acids along the casein chain prevents the diffusion of non-polar molecules through casein-based films. The later avoid oxygen to penetrate foods which are prone to oxidation reactions[281]. Even through casein-based films are sensitive to moisture thus decreasing seriously their mechanical properties, the addition of plastizers, crosslinkers[282-288] or the modification of casein network can reduce these inconveniences[289]. Unfortunately, as casein do not show any inherent antibacterial properties, and the addition of biocide agents such as EOs is of prime importance to obtain performing antibacterial materials (Table 27). Arrieta et al. evaluated the antibacterial effects of transparent bio-films based on plasticized caseinate derivatives with carvacrol on *E. coli* and *S. aureus* according to the agar diffusion method[290]. Sodium and calcium caseinates films incorporated carvacrol exhibit good antibacterial properties against both bacteria but *S. aureus* seems more sensitive to carvacrol than gram-negative one. Indeed, the inhibition zone diameter was evaluated at 7 mm for *S. aureus* whereas it drastically decreases between 2 and 4 mm with *E. coli*. Interestingly, the *E. coli* inhibition zone differs according to the nature of casein used. The authors suggested that the divalent calcium cations in calcium caseinates increase the crosslinking with protein chains, thus slowing down the diffusion of carvacrol outside the calcium caseinates films. Broumand et al. also demonstrated interesting antibacterial properties of sodium caseinate based edible films[291] elaborated by the emulsion-film producing method and incorporating *Zataria multiflora Boiss* EO. Results reveal that *S. aureus* are much more sensitive than *Salmonella typhimurium* and *E. coli* to EO with an inhibitory zone diameter of 25.17 mm, 17.62 mm and 15.2 mm, respectively. The higher resistance of gram negative against *Zataria multiflora Boiss* EO seems to be due to the weak rate of EO dissolution in the lipid phase of the bacteria membrane and to a different cell surface hydrophobicity as suggested by Lanciotti and coworkers[292]. Finally, Oussalah et al. investigated the antibacterial effect of oregano essential oil incorporated in calcium caseinate and whey protein isolate edible films[293]. Interestingly, more than 1 log reduction of *E. coli* and *Pseudomonas spp* were observed on the surface of beef muscle pieces. This study reveals that caseinate film provides good polymer network to release carvacrol and thymol (active antibacterial agents from oregano essential oil) that inhibit the growth of gram-negative bacteria.

The addition of EOs in casein-based films not only change their antibacterial properties but also modify their microstructural and mechanical properties (Table 28). For instance, the introduction of EOs into casein films increase the amorphous regions of film structure thus leading to more uniform, smooth, and less porous films in comparison with neat films[294-296]. Also, when emulsified oil droplets are introduced in casein films, structural discontinuation appears resulting in the decrease of TS and the Young's modulus, and the increase of EB. For instance, Aliheidari et al. reported that the incorporation of *Matricaria recutita* EO into casein-based films[297] reduced by 4.5 the TS value of casein film (2.5 MPa) compared to neat film (10.9 MPa). In some cases, EB % decreases as demonstrated by Broumand et al.[291] when incorporating *Zataraia multiflora Boiss* essential oil suggesting strong interaction between essential oil and casein matrix.

Table 27. Antibacterial properties of casein-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	Refs
Sodium caseinate (SC) and calcium caseinate (CC) matrices with glycerol and carvacrol	Carvacrol	*Escherichia coli, Staphylococcus aureus*	Agar disk diffusion method	290

Sodium caseinate films with stearic and oleic acids and *Zataraia multiflora Boiss* EO	*Zataraia multiflora Boiss* essential oil	*Escherichia coli, Staphylococcus aureus, Salmonella typhimurium*	Agar disk diffusion method	291
Milk protein-based films with oregano EO and pimento EO	Oregano ans pimento essential oil	*Escherichia coli, Pseudomonas spp.*	Counting method (dilution method)	293

Table 28. Mechanical properties of casein-based *Zataraia multiflora Boiss* EO films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Sodium caseinate (SC) films with stearic and oleic acids and *Zataraia multiflora Boiss* essential oil (ZEO)	**Films without** ZEO**:** 2.23 ± 0.20 MPa **Films with** ZEO**:** 1.94 ± 0.15 MPa	**Films without** ZEO**:** 745 ± 48 % **Films with** ZEO**:** 212 ± 41 %	291

3.6.3. Whey proteins

Whey proteins constitute the by-product of the cheese-making process and are defined as the remaining milk matter after coagulation of casein at pH 4.6 and 20°C[298]. The world annual global market of whey proteins is projected to reach the growth rate of 7.5% from 2018 to 2023, and the demand was evaluated at $9.4 billion in 2017[299]. the benefits of Whey proteins are such that they are used in many areas such as sports nutrition, confectionery, bakery, health foods, and recently in the synthesis of edible films and coatings for food protection[300]. Whey protein-based films exhibit not only good barrier properties against oxygen but also interesting mechanical and antibacterial properties when combined with essential oils (Tables 29 and 30). Seydim et al. studied the antimicrobial properties[301] of whey protein derived films containing 1.0–4.0% (wt/vol) ratios of oregano, rosemary and garlic EOs against *Escherichia coli* O157:H7, *Staphylococcus aureus*, *Salmonella enteritidis, Listeria monocytogenes* and *Lactobacillus plantarum*. 2% of oregano EOs was reported as the minimium concentration used to inhibit the growth of all the previously mentioned bacteria. As expected, the higher the concentration of OEO (4%), the greater the zone of inhibition. The inhibitory zones reach respectively 37.09 mm^2, 43.07 mm^2, 40.59 mm^2, 41.65 mm^2 and 13.45 mm^2 for *Escherichia coli* O157:H7, *Staphylococcus aureus*, *Salmonella enteritidis, Listeria monocytogenes* and *Lactobacillus plantarum.* On the contrary, and in the same experimental conditions, the introduction of 4% of garlic EOs did not show any significant antibacterial properties, and the maximum inhibitory area was observed with *Staphylococcus aureus* (13.45 mm^2). Indeed, diallyl disulfide (60%), diallyl trisulfide (20%) and allyl propyl disulfide (16%), the main components extracted from garlic EOs[302], are not fairly active toward *E. coli* compared to OREO[303]. Unfortunately, rosemary EO loose its known antibacterial activities when incorporated in whey proteins-based films. The later did not show any inhibitory effect against all tested bacteria. Unlike the results observed by Seydim and Sarikus[301], the minimum concentration of OREO required for inhibiting the target microorganism (*Penicillium commune*) in whey protein-based films in Oliveira et al. investigation[304] was evaluated at 1.5% with an inhibitory zone of 1.7 cm. Authors underlined the attractivity of whey protein isolate-based films incorporated with OREO for extending the shelf life of food products. Such observations are in agreement with Fernandez-Pan's study[305]. Indeed, the tested whey proteins-based OREO and CLEO films exhibited significant differences in antimicrobial effectiveness against total aerobic mesophilic bacteria, *Enterobacteriaceae*, lactic acid bacteria, and *Pseudomonas spp*. These results depend on (1) the nature of EO selected, (2) the concentration of EO introduced in the films, and (3) the tested microbial target. A higher antimicrobial activity is observed with OREO (carvacrol is the main active component) containing films as compared to those incorporated CLEO (eugenol is the main active compound). This finding is in total agreement with the related literature which recognized OREO as one of the most effective antimicrobial agents due to the presence of carvacrol and thymol[156]. Not surprisingly the inhibitory effect increases with OREO percentage content. In most of the cases, an evident antimicrobial activity was observed for the whey protein-

based films containing 30 g kg^{-1} of OREO. The range of surface inhibition was between 374 and 666 mm^2 for total aerobic mesophilic bacteria, between 165 and 650 mm^2 for *Enterobacteriaceae*, from 600 mm^2 to 900 mm^2 for lactic acid bacteria and from 50 to 175 mm^2 for *Pseudomonas spp.* This study also reflects the complexity of the interactions and sensitivity of microbial populations towards essential oils and their active compounds. In 2014, Bahram et al. investigated the antibacterial effects of cinnamon EOs-based whey protein films[306] against seven different pathogenic bacteria, including *Lactobacillus lactis*, *Pseudomonas putida*, *Streptococcus agalactiae*, *Escherichia coli, Listeria monocytogenes*, *Bacillus subtilis* and *Candida albicans*. Interestingly, and despite the weakness of the films by incorporating CEO, tremendous inhibition of zone areas were observed with those films against most of the bacteria strains. Authors consider that the diffusion of CEO through the films is responsible for bacterial inhibition as previously demonstrated against gram-positive and gram-negative bacteria[307-308]. Recently, Çakmak et al. introduced lemon and bergamot EOs in whey protein-based edible films for antibacterial applications[309] against *E. coli*, *S. aureus* and *Aspergillus niger*. According to disk diffusion method, *E. coli* seems to be more sensitive to both EOs than *S. aureus*, but no effect can be observed on *Aspergillus niger*. An average inhibition zone areas of about 26.62 cm^2 were obtained with *E. coli*; those inhibition areas are 100 times higher than that observed with *S. aureus*.

Regarding the mechanical properties, few studies investigated the mechanical properties of casein-based materials. For example the addition of OREO[304] (0.5 and 1wt% of OREO) promotes strong interactions with the side groups of the casein chains, leading to greater TS. However, the increase in OEO concentration from 1% to 1.5% resulted in a drop of the TS from 109 MPa to 92 MPa, likely due to a plasticizing effect caused by an “excess” of oil concentration. Surprisingly, the addition of CEO into casein matrix leads to a heterogeneous and « cracked » structure responsible for the significant decrease of TS and EAB values as previously described for gelatin-CEO based films[270].

Table 29. Antibacterial properties of whey-based EOs films

Film material	Essential oils	Bacteria strains	Experiments to prove antibacterial activity	*Refs*
Whey protein isolate (WPI) films with oregano, rosemary and garlic essential oils	Oregano, rosemary and garlic essential oils	*Escherichia coli, Staphylococcus aureus, Salmonella enteritidis, Listeria monocytogenes Lactobacillus plantarum*	Agar disk diffusion method	301
Whey protein films with oregano essential oil	Oregano essential oil	*Penicillium commune*	Agar disk diffusion method and quantification of colony-forming units	304
Whey protein films with oregano or clove essential oils	Oregano or clove essential oils	*Pseudomonas, Lactic acid bacteria, Aerobic mesophiles, Enterobacteriaceae*	Agar disk diffusion method	305
Whey protein films with lemon and bergamot essential oils	Lemon and bergamot essential oils	*Escherichia coli, Staphylococcus aureus, Aspergillus niger*	Agar disk diffusion method	309
Whey protein films with cinnamon essential oils	Cinnamon essential oils	*Lactobacillus lactis*, *Pseudomonas putida*, *Streptococcus agalactiae*, *Escherichia coli, Listeria monocytogenes*, *Bacillus subtilis* and *Candida albicans*	Agar disk diffusion method	306

Table 30. Mechanical properties of whey-based EOs films

Film material	*Tensile strength (MPa)*	*Elongation at break (%)*	*Refs*
Whey protein films with oregano essential oil	**Films without OREO:** 66 ± 5 MPa **Films with 0.5% of OREO:** 96 ± 3 MPa **Films with 1% of OREO:** 109 ± 7 MPa **Films with 1.5% of OREO:** 92 ± 8 MPa	–	304
Whey protein films with cinnamon essential oil	**Films without CEO:** 0.82 ± 0.09 MPa **Films with 0.8% of CEO:** 0.54 ± 0.01 MPa **Films with 1.5% of CEO:** 0.56 ± 0.04 MPa	**Films without CEO:** 36.58 ± 0.05 % **Films with 0.8% of CEO:** 26.36 ± 0.02 % **Films with 1.5% of OEO:** 34.9 ± 0.05 %	306

Conclusions

The combination of biobased polymers with essential oils is an interesting strategy for the development of antibacterial materials from bioresources to avoid the recurrent uses of petro-sourced or non-renewable resources. Depending on the concentration and the nature of the essential oils (EOs) tested, the antibacterial effects are variable. However, the higher the concentration of EOs, the more notable the antimicrobial effect. The nature of EOs is one of the key parameters not to be neglected since all the EOs do not have the same effectiveness on bacteria inhibition growth. Globally, gram-positive bacteria are more sensitive to active antibacterial molecules of EOs than gram-negative bacteria due to the structure of their membranes. It generally assumes that the cell wall of gram-negative bacteria is more complex than that of the gram-positive ones with the presence of a lipopolysaccharide layer surrounding a thin peptidoglycan layer. The combination of EOs with antibiotics or NPs may be a solution to enhance the antibacterial properties of EOs as previously described.

The polymer matrix is also an essential issue to consider: the more interactions exist between EOs and the polymer matrix, the less diffusion of the antimicrobial active species in the surrounding medium is observed, so that their antibacterial effectiveness decrease. This raises out the question of the influence of EOs on the mechanical strength of the materials. The strong interactions of some EOs with the polymer matrix by intermolecular hydrogen bonding generate crosslinks which decrease the free volume and restricts the molecular mobility of the polymer chains. This phenomenon led to a sheet-like structure where arrangement of stacking layers of EOs and polymer chains are possible, leading to a compact structure, thus increasing continuities within the polymer network: this results in the increase of TS and a decrease of EB. On the contrary, in some cases, the presence of a high amount of EOs may interrupt the continuity of the film microstructure, probably by decreasing hydrogen bonding between chains and chain entanglements, thereby declining the mechanical strength of the films. The addition of essential oils can therefore act as plasticizers, reducing the interaction between polymer chains and conferring more flexibility to the materials. Such a behaviour is of prime importance for antibacterial materials used as wounds dressings.

The idea of combining essential oils and bio-based polymers is an interesting strategy from an environmental point of view: petro-based polymers are replaced by polymers with similar properties. However, the antibacterial effect of these materials is limited in time. Indeed, EOs diffuse out of the materials to prevent the adhesion and the proliferation of bacteria on their surface. When the entire reservoir of EOs has been used, the materials no longer have obvious antibacterial activity; this has led scientists to use high concentrations of EOs, which could raise some problems of solubility and homogeneity of the final materials.

Last but not the least, the complexity of the composition of the different EOs, and their variations that could be significant inside a same EOs from different origins, act clearly as a brake on the identification of the mode of antibacterial action and the relative contribution of the major active compounds of EOs regarding to the antibacterial properties. Recent advances in genomics, including transcriptomic, proteomic and metabolomics, will certainly enhance our knowledge related to the mode of action of EOs and their biologically active components.

Future prospects

To design the most effective antibacterial materials, the scientific community should develop standardized antibacterial methods to easily compare the antibacterial effectiveness of the final materials. It appears very difficult to compare the antibacterial effect of materials when the methods and the nature of the tested bacteria differ from each study (disk diffusion method, counting method, inhibition area in mm^2, inhibition area in mm...).

The synthesis method of the antibacterial films should also be considered in the further experiments: indeed, the active compounds from EOs are volatile and the processability of the antibacterial materials at high temperature leads to the evaporation of EOs, and thus a lesser antibacterial effect. To overcome this issue, EOs could be incorporated into materials which synthesis through a photochemical process for example, under mild conditions at room temperature is possible. Depending on the degree of cross-linking of the photoinduced materials, the release of EOs could be easily controlled over time. EOs can also be functionalized with reactive functions such as acrylate, methacrylate, vinyl or epoxide groups. These derivatives could play pivotal role as photo-crosslinkable

monomers for the synthesis of innovative materials with long lasting antibacterial activity. Bacteria would be in direct contact with the phenolic groups of the active compound of EOs, increasing the antimicrobial efficiency over time. Such systems have gained increasing interests and may be the next generation of antibacterial materials : for example, Renard et al. used thiol-ene photoreactions to encapsulate tannic acid or carvacrol in eugenol-based photoinduced networks to develop a long-lasting antibacterial effect against *E. coli* and *S. aureus*[310]. Epoxy-eugenol monomer was also copolymerized with resorcinol diglycidyl ether under UV cationic polymerization to tailor the mechanical/thermal properties of the final films but also to provide them antibacterial activity[311]. A new methacrylated monomer based on myrcetol, an essential oil extracted from *Myrtus communis L*, served as a model for the synthesis of anti-adhesive films against *B. subtilis*[312]. Recently, unmodified eugenol was used as antibacterial agent and photo-crosslinkable monomer in a limonene-based system[313]. More recently, Langlois et al. successfully designed an innovative antimicrobial material by integrating linalool within an allyl-based PHA network by a photo-induced thiol-ene process[314]. Essential oils nano-emulsions may be also a valuable solution to increase the dispersibility of EOs into polymer matrix reducing their interaction with polymer chains, favouring their diffusion outside the materials. This technique may prevent thermo-oxidation reactions of EOs, enhancing thus their antimicrobial activity against bacteria. Also, nano-emulsions process is an interesting way to avoid the evaporation of EOs when processability of materials occurs at high temperatures. The potential use of essential oils nano-emulsion opens the field for new alternative treatments of natural origin in food and pharmaceutical industries[315-317], avoiding the antimicrobial resistance problems associated with the use of antibiotics. Further clinical studies on essential oils nano-emulsion formulations may broaden its potential as controlled drug delivery systems and could be used clinically in humans.

Conflicts of interest

"There are no conflicts to declare".

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Abbreviation list

Apricot (*Prunus armeniaca*) kernel essential oil: AKEO
Bane essential oil: BANEO
Bergamot essential oil: BEO
Black pepper essential oil: BPEO
Caraway essential oil: CAEO
Chamomile essential oil: COEO
Cinnamon essential oil: CEO
Clove essential oil: CLEO
Eucalyptus globulus essential oil: EGEO
Ginger essential oil: GEO
Lemongrass essential oil: LEO
Mentha pulegium essential oil: MEO
Orange essential oil: OEO
Oregano essential oil: OREO
Orange peel essential oil: OPEO
Peppermint essential oil: POEO
Rosemary essential oil: REO
Tea tree essential oil: TTEO
Thymol essential oil: TEO
Zataria multiflora Boiss essential oil: ZEO

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