CHAPTER

12 Nanocomposites using clove (*Syzygium aromaticum*) chemical constituents

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1. Introduction

Green chemistry has the opportunity to ensure that the world of chemistry produces more effective and efficient materials for various applications and contributes to protecting public health and the environment. Furthermore, the technology optimizes all necessary parameters to minimize if not eliminate environmental pollution either through the production of benign by-products or employing safe reactants and solvents, and minimizing packaging waste.

Nanocomposites are a heterogeneous combination of two or more materials to yield new materials with new and unique properties. The unique characteristics of the newly formed nanocomposites can be controlled and optimized by using an effective mixture of original components. As a result, the applications of nanocomposite materials are expanding rapidly in many fields (Shirdar et al., 2019; Nguyen-Tri et al., 2018).

The Food and Agriculture Organization (FAO) of the United Nations estimated that 30% of the produced food is lost or wasted each year because of improper storage. Generally, food loss occurs at the production, handling, storage, and processing levels, while food waste indicates the losses at distribution, market, and final consumer levels (Ishangulyyev et al., 2019; Jiang et al., 2019). The global food packaging market was estimated at over USD 300 billion in 2019 and had a predicted increase rate of 5.2% yearly. The paper-based segment represents 31.9% of the total value and dominates as a biodegradable material. On the other hand, plastic food packaging, which is mostly nonbiodegradable, is dominating the market due to superior properties and lower prices; however, it raises environmental concerns (Wohner et al., 2020) and encourages the search for new safe and renewable natural-based packaging materials. Therefore, it becomes necessary to pay considerable attention to the development of biodegradable materials prepared from natural polymers. Thus, various natural

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polymers are under study to develop improved products. In addition, many random research works have been documented in the literature on the development of biodegradable packaging film using renewable polymers (Shah et al., 2015; Tunma, 2018).

The market is shifting toward more sustainable packaging solutions like bio-based polymers (Wohner et al., 2020). The development of antimicrobial packages using natural agents such as clove oil is a promising path for actively controlling the bacterial and fungal proliferation that leads to food spoilage (Kerry et al., 2006; O'Callaghan and Kerry, 2014; Rai et al., 2019; Vilas et al., 2020). This type of package increases the latency phase and reduces the growth of microorganisms, enhancing the food quality and safety, ensuring a longer shelf life (Jayasena and Jo, 2013; Szabo et al., 2020; Motelica et al., 2020).

The clove essential oil (CEO) is an aromatic oil containing mainly eugenol (71.6%) and eugenol acetate (9.0%), while others have reported higher concentrations with the presence of β-caryophyllene as well. The various phytochemical compounds present exhibit a broad spectrum of pharmacological activities such as anticancer, antimutagenic, anti-inflammatory, antiallergic, antimicrobial, and antioxidant properties (Barboza et al., 2018). Such multi-pharmacological activities of the CEO give merits to be part of different nanocomposite packaging formulations that could enhance the food quality and can be employed in numerous applications.

2. Nanocomposites

The food industry containment has evolved to attract its customers, especially in packaging. The packaging technology has advanced to eliminate breakage and inhibit entry of moisture, oxygen, UV light, and movement of food solvent. Some natural films that have been used previously contain biodegradable polymers, waxes, polysaccharides, proteins, lipids, and/or a mixture. The research development in such lining can lead to edible films and coating to serve the current lifestyle of consumers. The design ensures that the inner lining further protects the food and reduces its oxidation process to warrant its safety. Thus, increasing shelf life and retaining the integrity of food's original taste. Food storage is crucial, and containers have improved over the years leading to various packaging technology.

Incorporating bioactive packaging that contains antimicrobial and antioxidant agents is beneficial compared to preservatives in the food industry. Preservatives can affect the flavor of the food; hence, natural alternatives would be desirable and safer. This is because they would be considered harmless given their natural origin and subsequently preserve the food. This has led to active packaging that provides passive protection that retains the food quality and further diminishes or hinders microorganisms' growth. The debatable controversy of butylated hydroxytoluene as a preservative due to its possible risks in cancer and asthma enables the utilization of CEO more attractive.

Antimicrobial in CEO activity equips the packaging material to inhibit the growth of microbial spoilage pathogens such as *Escherichia coli*, *Salmonella*, *Listeria monocytogenes*, *Staphylococcus aureus*, and *Bacillus cereus* (Liu et al., 2017). The phenolic compounds are multifunctional. They react with phospholipids of the microbial cell membrane that affects its porosity which denatures its proteins. β-Caryophyllene is the dominating nonvolatile compound in CEO possessing antioxidants property. It prevents the generation of free radicals produced during oxidation while the food deteriorates. It is, therefore, an ideal additive in food packaging as it can sustain the unique taste of food and inhibit the growth of food pathogens.

Polymers in food packaging have been designed to provide excellent barriers as they can be engineered to possess improved oxygen permeability and mechanical properties. This, however, has its drawback if affected during transportation which is overcome using CEO. However, phytochemical compounds that make CEO are volatile; hence, if added to packaging material, it is unstable to ensure that it retains its bioactivity. The volatility will diminish the antimicrobial and antioxidant activities over time, impeding the packaging material's efficiency and triggering food spoilage before the product reaches the final consumer. This drawback can be rectified if the EO is packaged within the packing inner lining in such a way that its volatility is reduced if not eliminated. This is achieved using nanotechnology to strengthen the existing properties of polymer by equipping with bioactive EO via the development of nanocomposites.

Polylactic acid (PLA) is a special renewable, biodegradable polyesters polymer with attractive thermoplastic, mechanical, and biological properties that has earned its approval by the US Food and Drug Administration in biomedical and packaging materials (Scaffaro et al., 2018). In the aforementioned applications, the development of polymeric systems with antimicrobial property reduces microbial growth. Treatment of such promising polymers with CEO is an attractive approach as it has previously been demonstrated to produce plasticized nanocomposite (Munteanu et al., 2018).

Functionalized electrospun PLA film was coated with a 100-nm-thick cationic chitosan layer encapsulated with CEO via coaxial electrospinning. The high phenolic content from the immobilized CEO resulted in synergistic and higher antibacterial activity against *E. coli*, *L. monocytogenes*, and *Salmonella typhymurium* (Lu et al., 2021). The study showed that EO added mechanical property in addition to bactericidal effects compared to the unloaded films. Thus, chitosan displays antimicrobial activity but lacks mechanical property. On the other hand, PLA lacks any mechanical activity, but EO introduces antimicrobial property and pronged shelf life and mechanical property upon loading.

A comparative study utilizing chitosan and polyvinyl alcohol (PVA) blended films was prepared via solvent casting and phase inversion (Antunes et al., 2021). The two hydrophilic polymers formed a potent blend due to hydrogen bonding from the abundant —OH groups. This, in turn, effectively encapsulated the CEO with further phenolic interaction, which displayed enhanced thermal property. In addition, the synergistic inhibitory effect of microbial growth against Gram-positive *Staphylococcus aureus* and Gram-negative *Pseudomonas aeruginosa* was observed via the agar diffusion test. The nano-biocomposites also displayed higher antimicrobial activity compared to the isolated polymers.

Spherical and stable chitosan nanoparticles between 40 and 100 nm were synthesized by a two-step process (Hasheminejad et al., 2019). First, to minimize the evaporation and oxidation, nanoencapsulation of CEO of this biopolymer was achieved via an oil-in-water emulsion and ionic gelation of emulsion droplets technique. Second, a controlled release with prolonged activity displayed enhanced antifungal activity against *Aspergillus niger*. Similarly, chitosan nanoparticles and clove oil nanobiocomposites displayed superior antifungal activity against postharvest pathogenic fungus *Pythium aphanidermatum* (Radhakrishnan et al., 2021).

Another reinforcement of CEO nanoencapsulation with a potato-starch material was recently employed via 3D nanonetwork (Fang et al., 2020). The resultant nanocomposite possessed improved stability against thermal treatment and prolonged antimicrobial activity against Gram-negative bacteria (*E. coli*, ATCC 35150) and Gram-positive bacteria (*Bacillus subtilis*, ATCC 6633, and *Staphylococcus aureus*, ATCC 25923). This makes CEO a promising biomolecule in bacterial and fungal infection in medical, food, and agriculture industries.

Eugenol is the principal constituent of CEO and is widely used in food, pharmaceutical, cosmetics, and active packaging applications, owing to its effective antimicrobial and antioxidant properties (Baskaran et al., 2010; Devi et al., 2010). However, most plant-derived bioactive compounds, including eugenol, are highly volatile, unstable, and sensitive to oxygen, light, and heat during processing, utilization, and storage (Choi et al., 2009; Garg and Singh, 2011; Gaysinsky et al., 2005). Therefore, eugenol is a good candidate as an antioxidant for various thermal processing applications, including bioactive plastics for food packaging. The thermal stability of eugenol has been improved by encapsulation into chitosan nanoparticles through a two-step method, i.e., the formation of an oil-in-water emulsion and the ionic gelation of emulsion droplets. The extrusion of eugenol-loaded chitosan nanoparticles and thermoplastic flour, a model plastic, at a temperature up to 155°C confirmed the improved thermal stability of encapsulated eugenol compared with nakedness eugenol (Woranuch and Yoksan, 2013). Furthermore, the emulsion-diffusion has been used as an effective method to improve the oxidation stability of eugenol; the compound was encapsulated by inclusion with β-cyclodextrin to be protected from light oxidation during storage time due to their complete wrapping of eugenol by polycaprolactone layer (Choi et al., 2009).

Lee et al. (2018) developed chitosan-based films containing CEO as an active agent by incorporating halloysite nanotubes (HNTs) to stabilize the oil droplets and reported their application as food packaging materials. Furthermore, they suggested that such films containing natural ingredients have the potential to be applied as active packaging solutions in food packaging systems due to their antioxidant and antifungal properties alongside their enhanced barrier property against water vapor (Lee et al., 2018). Chitosan nanoparticles loaded with CEO are very well-known for their antioxidant and antimicrobial activities; therefore, they have been applied in the food industry for food safety purposes (Hadidi et al., 2020). In addition, a recent study on the eugenol microemulsion reinforced with silver nanocomposite electrospun mats was developed for wound dressing applications (Sethuram et al., 2021).

3. Conclusions

Postharvest loss caused by microorganisms is considered a significant problem in the food industry. The recent packaging sector trends focus mainly on developing active packaging materials with inherent antimicrobial and improved barrier properties. The antimicrobial activity of the CEO is well known and documented, and it contributes to the final aims of the packaging materials as a protective layer against the microbial attack. Eugenol and CEO have been integrated into different polymers such as polylactic acid, PVA, potato-starch based, and chitosan in composite to produce effective and safe packaging materials; as the environmental impacts increase, the biodegradable natural components in the food industry become an urgent task. The efficiency of CEO nanocomposite was found to have the utmost potential as antimicrobial packaging material to ensure food safety by enhancing the shelf life and preventing postharvest loss. However, more research needs to be conducted to reveal the potential of the CEO as an effective component in food packaging due to the availability, safety, and intense antibacterial activity, and its major component, eugenol.

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