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Review Paper/Derleme Makale

Use of modified polycaprolactone polymer in food packaging applications: a review

Modifiye polikaprolakton polimerinin gıda ambalajlama uygulamalarında kullanımı: bir derleme

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Abstract

Objective: Plastic production in the world is constantly increasing and plastics have been degraded in nature for many years. This situation turns into a major environmental disaster that people and living organisms will encounter. In addition, packaging films that can be applied to foods safely and extend the shelf life of foods with their functional properties are needed. Polycaprolactone (PCL) is a biodegradable polymer produced by synthetic processes and has been frequently investigated in food packaging studies in recent years. Due to its flexibility, biocompatibility and thermoplasticity, the use of PCL and its copolymers in packaging film applications is becoming widespread. Disadvantages such as low mechanical and thermal resistance can be eliminated by adding fillers, mixing with other polymers or using multi-layers. This study aims to compile recent studies on the use of PCL polymer modified by various methods as food packaging.

Conclusion: In the literature, there are many interesting studies on the making composite of PCL with different methods. Nanoclays to improve mechanical and gas barrier properties; nanometals and plant materials to impart antimicrobial properties; innovative additives such as oxygen scavengers, photosynthesizing agents, antimicrobial peptides are used in the modification of PCL. In this review, it was revealed that the modifications contribute to PCL polymer in terms of stiffness and gas barrier properties and add antimicrobial and antioxidant character to the polymer.

Keywords: Polycaprolactone; biodegradability; packaging; biopolymers; modified films

Öz

Amaç: Dünyada plastik üretimi sürekli olarak artmakta ve plastikler uzun yıllar boyunca doğada bozunmaya uğramaktadır. Bu durum insanların ve canlıların karşılaşacağı büyük bir çevre felaketine dönüşmektedir. Bunun yanında fonksiyonel özellikleriyle hem gıdalara güvenli bir şekilde uygulanabilen hem de gıdaların raf ömrünü uzatabilen ambalaj filmlerine ihtiyaç duyulmaktadır. Polikaprolakton (PCL) sentetik süreçlerle üretilen ve son yıllarda gıda ambalajı çalışmalarında sıklıkla araştırılan biyobozunur yapıdaki bir polimerdir. Esnekliği, biyouyumluluğu ve termoplastik oluşu nedeniyle PCL ve kopolimerlerinin ambalaj filmi uygulamalarında kullanımı yaygınlaşmaktadır. Mekanik ve termal dayanımının düşük olması gibi dezavantajları dolgu maddeleri ekleme, diğer polimerlerle karıştırma veya çok katmanlı kullanımları ile giderilebilmektedir. Bu çalışmada, çeşitli yöntemlerle modifiye edilmiş PCL polimerinin gıda ambalajı olarak kullanımı ile ilgili son yıllarda yapılan çalışmaların derlenmesi amaçlanmıştır.

Sonuç: Literatürde PCL’nin farklı yöntemlerle kompozit haline getirilmesi ile ilgili pek çok ilgi çekici çalışma yapılmaktadır. Mekanik ve gaz bariyer özelliklerini geliştirmek için nanokiller; antimikrobiyal özellik kazandırması için nanometaller ve bitkisel materyaller; oksijen süpürücüler, fotosentezleyici maddeler, antimikrobiyal peptitler gibi yenilikçi katkılar PCL’nin modifikasyonunda kullanılmaktadır. Bu derleme çalışmasında, yapılan modifikasyonların PCL polimerine rijitlik ve gaz bariyer özellikleri açısından katkı sağladığı ve polimere antimikrobiyal ve antioksidan karakter kattığı ortaya konulmuştur.

Anahtar kelimeler: Polikaprolakton; biyobozunurluk; ambalaj; biyopolimerler; modifiye filmler

1. Introduction

Nowadays, the use of plastic in every field of life causes serious plastic pollution. The packaging industry, which accounts for 40% of the total plastic consumption, has the largest share in plastic waste production, especially with single-use packaging. Polymers such as polyethylene (PE), polyvinylchloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyamide (PA) are produced continuously due to their advantages in terms of mechanical, gas permeability, thermal stability and low-cost properties. These polymers cause many environmental problems because they are not biodegradable and recycling is insufficient. This situation prompted researchers to develop alternative materials to overcome these disadvantages (Siracusa et al., 2008). For this reason, there has been a trend towards developing of aliphatic polyesters that can be economically decomposed and biodegraded in waste facilities (Lim and Thian, 2022).

Biopolymers are divided into different categories according to the origin of the raw materials and their production processes. Plant carbohydrates include starch, cellulose, chitosan, agar, etc.; animal or plant proteins include soy protein, corn zein, wheat gluten, gelatin, collagen, whey protein, casein etc.; synthetic biodegradable polymers include polylactic acid (PLA), polyglycolic acid (PGA), poly(ε-caprolactone) (PCL), polybutylene succinate (PBS), polyvinyl alcohol (PVA), etc.; biopolymers produced by microbial fermentation include polyhydroxyalkanoates (PHAs) such as poly(β-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalera) (PHBV) (Rhim et al., 2013). PCL, a synthetic biodegradable polymer, is an aliphatic polyester containing hydrolyzable ester groups that promote its biodegradability. These ester groups are naturally compatible with microbial enzymes sensitive to catalytically triggered hydrolytic degradation of polymeric chains of PCL (Ilyas et al., 2022). As a synthetic biodegradable biopolymer not found naturally, PCL has been identified for its commercial potential. PCL is one of the earliest synthesized polymers by the Carothers Group in the early 1930s (Carothers et al., 1932).

Unlike traditional plastics such as polypropylene (PP) and polyethylene (PE), which take hundreds or even thousands of years to degrade fully, PCL biodegrades in just a few years. Due to their excellent biocompatibility, flexibility and thermoplasticity, PCL and its copolymers have been proposed for use in a variety of biomedical and biomaterial applications, resulting in many commercially successful applications (Ludueña et al., 2011; Mohamed and Yusoh, 2015). Besides, PCL is widely used in medical tissue engineering, drug delivery and controlled release systems, food packaging industry, antibacterial studies, protective clothing manufacturing and biosensors (Zhang et al., 2019). Despite its high cost, PCL is heavily used in food packaging research. The most significant known disadvantages are degradation due to low melting temperature and low mechanical strength. The most convenient and effective method to improve the mechanical properties of PCL and increase its potential usability in packaging applications is to reinforce the structure with fillers (Reis et al., 2021). While many biodegradable polymers have been studied as packaging materials in laboratories, few have been commercially applied. PCL and PLA are among the limited polymers applied. While PCL is used as an additive to facilitate the processability of other polymers, it can also be used alone as an alternative to polyolefins. PCL polymers are mixed with other polymers to improve their thermal, viscoelastic or mechanical properties. Since PCL is not as resistant to high temperatures and mechanical effects as other polymers, mixing with other polymers may become necessary. Some transesterification agents can also harmonize immiscible polymers (Guarino et al., 2017). Some kind of polymers such as starch (Guarás et al., 2015), chitosan (Sarasam et al., 2006), glucomannan (Harsojuwono et al., 2022), polyethylene glycol (PEG) (Ortega-Toro et al., 2016), cellulose (Amini et al., 2023), PLA (Chavalitpanya and Phattanarudee, 2013), cyclic olefin copolymer (COC) (Sogut et al., 2021) etc. can be used as a blend with PCL.

PCL can also be used in some multi-layer film production applications due to its properties. Multifunctional packaging materials can be produced by combining two or more layers and modifying these layers with various substances (Takala et al., 2013). The formation of a multi-layered structure of two different polymers is important in terms of improving the surface properties of the film and combining the unique properties of both polymers. Food packaging production using the combination of polymers decreases the level of toxic chemicals implicitly (Mahieu et al., 2017). For example, PCL shows excellent properties against water vapor, while starch shows this property against atmospheric gases. By forming a multi-layered film of these two polymers, barrier properties against both water vapor and gases can be achieved (Ortega-Toro et al., 2015). Recycling is more difficult due to the coexistence of different polymers in multi-layered food packaging. Biodegradable polymers offer a recycling advantage in this regard. If one of the layers is a biodegradable polymer such as PCL, this dramatically simplifies the recycling process (Reščeк et al., 2016).

Since the environmental value of biodegradable materials has been understood in recent years, many studies have been carried out on PCL. The development of composite technology has also made it easier to progress in this regard. In this study, we aimed to review the latest researches on modified PCL polymer in food packaging applications. Biodegradable materials were reviewed at different studies before, nevertheless this study focused on the recently worked innovative functional agents and their characteristics in the PCL food packagings. Based on our knowledge, most of the review papers addressed tissue engineering, drug delivery systems, biomedical applications, scaffolds etc., therefore this review contribute literature in terms of food packaging applications. Similar agents were classified in the text according to their functions in PCL films. In addition, general information is given about the structural properties, biodegradability and composite properties of PCL.

2. Properties and use of PCL

2.1. Physical and chemical properties

PCL is a semi-crystalline, hydrophobic and synthetic aliphatic polyester composed of repeating hexanoate units (Sachan et al., 2023). Among the biodegradable polymers, aliphatic polyesters such as PCL are now commercially available and are an interesting alternative to conventional thermoplastics. PCL can be synthesized by ring-opening polymerization (ROP) of ε-caprolactone monomers, the free radical ROP of 2-methylene-1-3-dioxepane, or the condensation of 6-hydroxycaproic acid with various anionic, cationic and coordination catalysts. PCL is a highly crystalline semi-crystalline polymer that reaches 69% crystallinity but decreases at higher molar masses (Beltrán et al., 2014; Guarino et al., 2017). The chemical structure and synthesis methods of PCL are shown in Figure 1 and Figure 2, respectively.

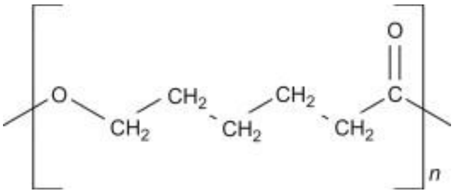

Figure 1. Structure of poly(ε-caprolactone) (Guarino et al., 2017)

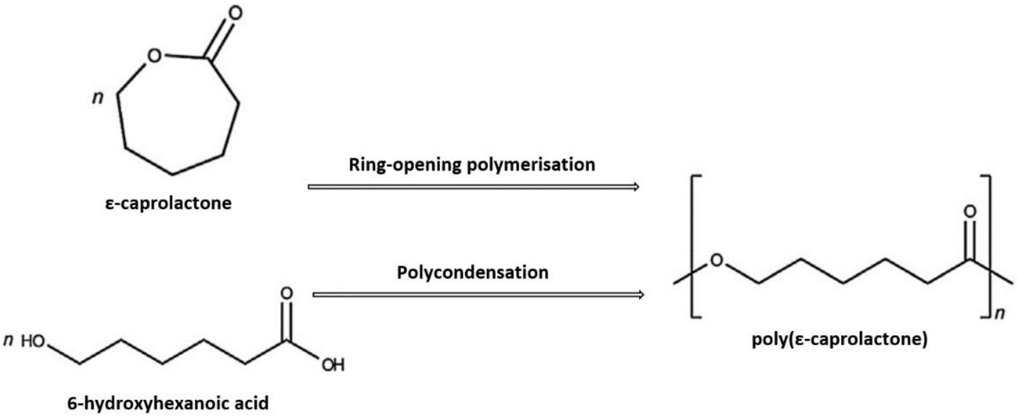

Figure 2. Synthesis methods of poly(ε-caprolactone) (Bartnikowski et al., 2019)

PCL is a hydrophobic and thermoplastic polymer with low water adsorption, resistant to UV rays and chemicals. These properties make it a suitable candidate for food packaging material (Reshmi et al., 2017; Paula et al., 2019). The physical, thermal and mechanical properties of PCL vary according to its molecular weight and degree of crystallinity, as shown in Table 1. It dissolves at room temperature in chloroform, dichloromethane, carbon tetrachloride, benzene, toluene, cyclohexanone, and 2-nitropropane. It is slightly soluble in acetone, 2-butanone, ethyl acetate, dimethylformamide and acetonitrile, but insoluble in alcohols, petroleum ether, diethyl ether and water. Blends of PCL with polymers such as PE, PP, natural rubber, polyvinyl acetate are mechanically compatible (Labet and Thielemans, 2009).

Table 1. Properties of PCL (Labet and Thielemans, 2009)

Properties	Range
Average molecular weight (M_n/g mol^{-1})	530–630000
Density (ρ/g cm^{-3})	1.071–1.200
Glass transition temperature (T_g/°C)	(-65)-(-60)
Melting temperature (T_m/°C)	56–65
Decomposition temperature (°C)	350
Internal viscosity (η_{inh}/cm^3 g^{-1})	100–130
Actual viscosity (η/cm^3 g^{-1})	0.9
Tensile strength (σ/MPa)	4–785
Young modulus (E/GPa)	0.21–0.44
Elongation at break (ε/%)	20–1000

2.2. Biodegradability of PCL

In the 1980s, scientists began investigating whether plastics could be designed to be susceptible to microbial attack. Biodegradation is about specially designed polymers to break down into their monomers under some circumstances. This phenomenon, also called biotic degradation, occurs when microorganisms such as bacteria, yeast, mold and algae chemically degrade polymers. Polymeric materials are not readily biodegradable. The degree of crystallinity of the polymer has a negative effect on degradation (Cesur, 2018). In addition to being a difficult process for the polymer to degrade in nature, it depends on conditions such as temperature, humidity, pH, UV rays, and microbiota (Guo et al., 2012). The small polymer particles formed after the reduction in the molecular weight of the biodegradable polymer and subsequent macroscopic structural deterioration are completely metabolized by cells or microorganisms. PCL's biodegradable properties are affected by its amorphous structure, as a result of DSC analysis, it has been determined that the amorphous part of PCL is used first during degradation and its crystallinity gradually increases (Khatiwala et al., 2008). Biodegradable polymers such as PCL are produced by conventional synthesis of synthetic monomers derived from sources such as petroleum. Microorganisms found in nature contain enzymes that break specific bonds between these monomers (Kılınç et al., 2017). Biodegradable polymers are generally degraded by microorganisms and chemical reactions in aquatic and terrestrial environments. The rate of degradation is sensitive to the microorganism population in the environment, humidity, temperature and oxygen (Yang et al., 2010). PCL generally degrades in nature in 2 to 4 years, depending on its molecular weight. Polymers containing ester groups, such as PCL, are susceptible to hydrolysis by chemical or enzymatic means. Degradation of PCL can occur in many ways: radical-induced, thermal, pH-induced, enzymatic, and intracellular. Lipases secreted by bacteria of the genus *Pseudomonas* and *Lactobacillus* are among the most effective in breaking down both amorphous and crystalline regions. Fungal lipases secreted by *Thermomyces*, *Candida*, *Aspergillus*, *Mucor* and *Rhizopus* genera are also effective on amorphous structure (Bartnikowski et al., 2019).

2.3. Composite PCL films

The primary purpose of active packaging technologies is to change the conditions of packaged foods to extend their shelf life. This practice can improve food safety and sensory properties while maintaining the quality of packaged food (Sanchez-Garcia et al., 2008). Especially consumable or biodegradable materials can extend the shelf life of foods without harming the nature. These materials not only act as a moisture and gas barrier, but also add different protective functions to the packaging film by containing a wide variety of additives such as antioxidants, antimicrobials, pigments, sweeteners, spices (Salmieri and Lacroix, 2006). PCL can be applied to packaging to prevent some packaging materials from coming into direct contact with food, as well as to increase the distance entrapped active compounds have to travel to reach the food surface and facilitate slow release into food (Mugwagwa and Chimphango, 2020). PCL also helps to reduce the amount of waste packaging in nature by adding biodegradability to modified atmosphere packaging (MAP) systems (Makino and Hirata, 1997).

Composite packaging films with controlled release are new generation packaging materials that can release active compounds at different rates in order to increase the quality and safety of foods during long-term storage. The inclusion of antimicrobial substances in packaging allows the gradual transfer of antimicrobials to food during storage and distribution. Antimicrobial packaging is suitable for variety of food stuff as meat, fruit, vegetables, etc. It effectively minimizes the surface microorganism load of foods (Sanchez-Garcia et al., 2008). This technology responds to consumer demands for less processed, natural and preservative-free food products. Antimicrobial agents include organic acids, natural extracts, antibiotics, triclosan, essential oils, polymers (e.g. chitosan), bacteriocins (e.g. nisin), fungicides (e.g. benomyl), silver compounds (Bastarrachea et al., 2011). In addition, fillers such as nanoclays are added to eliminate the relatively weak mechanical and gas barrier disadvantages of PCL. The incorporation of exfoliated nanoclays into the PCL matrix improves the physical properties of the films. For example, when less than 10% by weight montmorillonite (MMT) is added to the PCL film, the stiffness, thermal stability and gas barrier properties of PCL films increase (Sanchez-Garcia and Lagaron, 2010). However, its poor thermal and mechanical resistance and limited gas barrier properties limit the use of PCL as a polymer matrix (Lee and Kim, 2010). For this reason, mechanical and gas barrier properties are improved by adding some fillers to its structure (Khalid et al., 2018). In addition, to overcome these disadvantages, a polymer matrix is developed by adding chemicals such as hydrocolloids, plasticizers, emulsifiers or surfactants to the structure of some biodegradable materials (Pineros-Guerrero et al., 2021). In particular, amphiphilic surfactants and emulsifying agents such as Tween 80 can provide more effective mixing of biodegradable polymers with hydrophobic matrices such as PCL and hydrophilic matrices such as chitosan (Gomes et al., 2021).

Composites can be obtained by various methods such as melt intercalation, compression molding, solvent dissolving, in-situ polymerization, and direct mixing of polymer and fillers. Since PCL melts quickly at 60°C, melt intercalation may be preferred over solvent dissolving method (Sachan et al., 2023). The electrospinning technique, developed as an alternative to conventional packaging film production, is a technology designed to manufacture nanofiber films with high porosity and specific surface area. These nanofibrous films allow for active and intelligent packaging applications due to the possibility of transporting bioactive compounds (Zou et al., 2023).

2.3.1. Nanoclays

In order to improve the mechanical, thermal and antimicrobial properties of PCL films, there are many studies with organomodified or non-organomodified nanoclays. When MMT nanoclay organomodified with cetyl trimethyl ammonium bromide (CTAB) was added to the PCL film, it gave better thermal and mechanical results than the non-organomodified version. It has also been reported that organomodified MMT nanoclay exhibits antimicrobial activity in PCL film in contrast to non-organomodified MMT nanoclay (Seyrek et al., 2021). In the study of Cesur et al. (2018), composite films were obtained by adding organomodified MMT nanoclay and chitosan with methyl dihydroxyethyl ammonium bromide (MDEB) surfactant to impart antimicrobial character to PCL. It has been observed that pure PCL does not show antimicrobial properties. Still, when 25% chitosan and 0.4% nanoclay are added, it has an antimicrobial effect on *Escherchia coli (E. coli), Pseudomonas aeruginosa* and *Clostridium albicans*. The addition of chitosan increases the biodegradability of composite films while decreasing their mechanical strength (Cesur et al., 2018). In a study, PE films were coated with PCL using the surface spread technique. Magnetite and casein were added to PCL to improve mechanical and barrier properties. Magnetite and casein alone and together significantly reduced the oxygen permeability of the film. While PE/PCL film showed lower tensile strength than PE film, magnetite and casein added increased the tensile strength (Reščеk et al., 2016).

The effect of modified PCL films on meat and meat products that are perishable by microorganisms is an important research topic. It was reported that PCL/PHB/Cloisite® 30B and 10A nanoclay composite and nisin as an antimicrobial agent increased the shelf life of hams inoculated with *Lactobacillus plantarum* (Correa et al., 2017). In another study, the effect of PCL nanocomposite films containing organomodified halloysite (HNT) and MMT nanoclays and silver ions on the microbiological quality of ground beef was investigated. It has been reported that total mesophilic aerobic, lactic acid and total coliform bacteria loads in minced meat samples were lower in nanocomposite PCL films compared to pure PCL and low-density polyethylene (LDPE) films after eight days of cold storage at 4°C (İlaslan et al., 2022). Vermiculite nanoclay can intercalate active ingredients with its highly negatively charged layers. In a study in which antifungal ciclopirox olamine (CPO) and zinc oxide (ZnO) were intercalated into vermiculite and PCL was used as the polymer, the growth of *E. coli*, *Staphylococcus aureus (S. aureus)* and *Candida albicans (Can. albicans)* was inhibited. It was stated that the inhibition effect of CPO increased with ZnO content (Holešová et al., 2021). Layered double hydroxides (LDH) are brucite-like structures consisting of positively charged metal hydroxide layers and containing anionic ions (such as CO_3^{2-}, Cl^-, NO_3^-) in the gallery spaces. These anionic structures can take potentially active molecules into their form through the ion exchange mechanism. It was observed that the water vapor barrier property of PCL was improved by adding the 2-ethylhexanoate-conjugated phosphonium cation as a surfactant to the LDH (Lins et al., 2018).

2.3.2. Nanoparticles

In a study by El-Naggar et al., copper nanoparticles (Cu-NP) were myco-synthesized using *Aspergillus terreus (A. terreus)* AH20. Antimicrobial film was obtained by adding Cu-NP to cellulose acetate/PCL films. The films show antimicrobial effect on *E. coli, Pseudomonas aeruginosa, S. aureus, Bacillus subtilis*, *Can. albicans*, *Aspergillus niger, A. terreus, Penicillium expansum* and *Fusarium oxysporum*. In addition, both the mechanical and air permeability properties of the films were improved with Cu-NP (El-Naggar et al., 2022). It has been reported that PCL/ZnO nanocomposite film, prepared by in-situ ROP of ε-caprolactone, passes 46% less water vapor than pure PCL film, has better antimicrobial properties against *E. coli*, and increases the rate of biodegradation (Bujok et al., 2021). Titanium oxide nanoparticles (TiO_2-NP) can be added to polymers due to their antimicrobial properties. Because TiO_2-NP is inert, inexpensive and non-toxic, it has a wide range of uses such as cosmetics, food packaging, toothpastes, and pharmaceuticals (Muñoz-Bonilla et al., 2013). In a silver nanoparticle (Ag-NP) study, lipase from *Lactobacillus amylovorus* was used for immobilization on the PCL surface. Ag-NPs bound by lipase molecules effectively inhibited *E. coli* (Maroju et al., 2021). In another study using kaolinite and Ag-NP intercalated with dimethyl sulfoxide (DMSO) as additives, both the barrier properties of PCL film and its antimicrobial effect on *S. aureus* and *E. coli* were increased. The antimicrobial effect was achieved through the controlled release of Ag-NPs (Benhacine et al., 2019).

2.3.3. Plant sources

In recent years, adding substances obtained from plant sources to polymers used in food packaging has been a frequently researched subject. These bioactive compounds in polymers show their antimicrobial and antioxidant properties with controlled release and increase shelf life. Many plant-derived substances such as curcumin (Cai et al., 2022), quercetin (Rojas et al., 2021), green tea extract (Shahrampour et al., 2023), *Moringa oleifera* leaf extract (Núñez-Gastélum et al., 2019), linalool (Li et al., 2022), β-caryophyllene (Ullah et al., 2023), pomegranate peel extract (Khodanazary, 2019), soy protein isolate (Wu et al., 2019), babassu epicarp and mesocarp (Reul et al., 2019), rice straw fiber (Wu and Liao, 2012), grapefruit seed extract (Wang et al., 2019) can be added to the PCL.

Fiber films prepared with konjac glucomannan, PCL and Ag-NP using electrospinning method effectively inhibited *S. aureus* and *E. coli* (Lin et al., 2020). In a study in which essential oregano oil-loaded β-cyclodextrins were incorporated into PLA/PCL nanofibers, it was revealed that essential oregano oil was released from nanofibers for a long time and continuously. Nanofibers delayed postharvest rotting, spoilage and nutrient loss of blackberry. β-cyclodextrins loaded with essential oregano oil increased the thermal stability of the nanofibers and decreased the tensile strength (Shi et al., 2022). PCL/gelatin electrofiber films containing essential cumin oil (ECO) and ZnO nanoparticles (ZnO-NP) slowed down the growth of *S. aureus* in cheese during 12 days of cold storage. In addition, it was observed that ECO/ZnO-NP added to the film at a rate of 3% improved the tensile strength, elongation at break and Young's modulus properties (Shanbehzadeh et al., 2022). Green tea essential oils enhanced the antimicrobial and antioxidant properties of the film when incorporated into PCL/casein nanofibers (Yavari Maroufi et al., 2022).

In a study using PCL and starch to produce a biodegradable film, pomegranate peel was used to impart antimicrobial properties. The bioactive compounds in the pomegranate peel added to the film gave the film an antimicrobial property. The addition of starch to PCL increased the rigidity of the film while increasing the release rate and antimicrobial properties of bioactive compounds (Khalid et al., 2018). In another study using pomegranate extract, dried pomegranate seeds and pomegranate seed flour as additives in PCL, the growth of *E. coli* and *S. aureus* growth was slowed down (Uzunlu and Niranjan, 2017).

PCL nanofiber mats added 9% by mass from the antimicrobial *Acalypha indica* leaf extract showed an effective inhibition on Gram-positive and Gram-negative bacteria (Mathiazhagan et al., 2021). A functional biodegradable film was obtained by adding green tea extract, which is a natural antioxidant source, to the PCL/PLA composite film. In the study, the addition of green tea extract to the film made the structure more permanent due to the polyphenol substances it contains. Therefore, the water vapor and oxygen permeability of the film is reduced, while its mechanical and biodegradable properties are improved (Sadeghi et al., 2022). In a study in which antimicrobial-effective grape seed extract (GSE) was added to the PCL/chitosan film, the effect of the molecular weight of chitosan on the release rate was investigated. Low molecular weight chitosan caused a faster release of GSE (Lim and Thian, 2022). In a similar study, PCL/chitosan/nanocellulose composite films containing GSE improved the microbial quality of chicken breast during storage (Sogut and Seydim, 2019). In another study, GSE added to PCL/chitosan/nanocellulose film increased the water permeability of the film, but phenolics such as catechins, epicatechin, gallic acid and procyanidins contained in GSE gave the film antimicrobial properties (Sogut and Seydim, 2018).

PCL/chitosan/rutin (a kind of plant flavonoid) nanofiber films have been found to reduce the microbial load of rainbow trout compared to pure PCL film (Piri et al., 2021). PCL containing 7% by mass of black pepper oleoresin was layered on the gelatin film by electrospin method. Multilayer gelatin coating with PCL improves gas barrier and mechanical properties, while the oleoresin effectively inhibits *S. aureus* (Figueroa-Lopez et al., 2018). Chlorogenic acids, including caffeic and quinic acids, are natural bioactive compounds of plant origin and can be added to packaging materials due to their antioxidant and antimicrobial properties. Chlorogenic acids added to PCL/polyvinyl pyrrolidone (PVP) nanofibers showed an inhibitory effect on *E. coli* and *S. aureus*, but this effect was not observed in nanofibers using only PVP. PCL eliminated the weak encapsulation ability of PVP, resulting in better uptake of chlorogenic acids into the structure (Cao et al., 2022).

Pectin, a natural polymer obtained from fruits such as apples and oranges, can be easily degraded by the effect of temperature under normal conditions and is difficult to process without additives. Materials such as pectin, which can be obtained from wastes, can be added to biodegradable polymers to bring environmentally friendly packaging. In a study, PCL was modified with maleic anhydride, benzoyl peroxide and glycidyl methacrylate and then mixed with pectin. PCL has added elasticity to the harder pectin due to its flexible structure. In addition, the gas barrier property of the film has improved compared to pure pectin (Gorrasi et al., 2021).

2.3.4. Alternative modification methods of PCL polymer

In the study of Choi et al. (2021), the PCL surface was first hydrolyzed with NaOH to form carboxyl groups on the surface. It was then activated with N-hydroxysulfosuccinimide (sulfo-NHS) and 1-ethyl-3-[3 dimethylaminopropyl]carbodiimide hydrochloride (EDC) so that T4 bacteriophages can bind to the surface. EDC/NHS-activated PCL film interacted with T4 bacteriophage. PCL films that interacted with T4 bacteriophages were found to be 30 times more effective on *E. coli* O157:H7 inoculated into beef than films physically adsorbed on the surface (Choi et al., 2021).

It was found that 0.1, 0.5, and 1% by mass thermally exfoliated graphene oxide added PCL films showed higher tensile strength than pure PCL film. PCL-graphene oxide nanocomposite films showed a bactericidal effect on *S. aureus* (Malik, 2022). In sensor fabrication, nanofiber materials are widely researched due to their high surface-to-volume ratio and 3-dimensional structure (Yang et al., 2020). A sensor prepared by adsorbing graphene oxide on PCL nanofibers was used to detect bisphenol A (BPA), a dangerous compound for humans, by voltammetric method (Furquim et al., 2020).

Antioxidant agents can also be added to PCL. In a study by Amorim et al. (2022), nanofibers were obtained by adding the flexirubin pigment produced by *Chryseobacterium shigense* bacteria into polyvinyl alcohol/kefiran/PCL. The resulting films reduced the enzymatic browning of apple slices (Amorim et al., 2022). Sensors can be produced by adding pigments sensitive to pH change into nanofibers. By adding 3% by mass of anthocyanin into PCL/PEG nanofibers, the pH decrease caused by microorganisms over time could be detected depending on the color change (Guclu et al., 2023). Photodynamic sterilization becomes possible by adding various photosynthesizing agents to PCL films. Photosynthetic substances produce reactive oxygen species (ROS) at specific wavelengths and cause oxidative damage to microorganisms. Since this method does not require high temperatures or chemicals, it does not reduce the nutritional value of the food. For this purpose, the metal-organic skeleton (MOF-545) containing porphyrin as a photosynthetic substance in the structure of PCL was used in the study. *E. coli* and *S. aureus* inhibition was achieved by using LED irradiation and the shelf life of the sliced apple was significantly increased (Zhao et al., 2022). In another study, pH and light-sensitive composite films were obtained by adding curcumin nanoparticles encapsulated with zeolitic imidazolate into PCL, and it was reported that these films photocatalytically inactivate *E. coli* and *S. aureus* bacteria. Activated under blue light, curcumin showed a strong antimicrobial effect by producing singlet oxygen and releasing zinc ions in an acidic environment (Cai et al., 2021).

By adding ascorbic acid, iron powder and copper chloride ($CuCl_2$) into PCL films, the films also gain the ability to scavenge oxygen in the package. This application can be beneficial to increase the shelf life and the quality of foods susceptible to oxidation (Mahieu et al., 2015). Sodium metabisulfite (SM) has oxygen scavenging, antioxidant, anti-browning, antimicrobial and antiseptic properties and is generally considered safe by the FDA, making it a candidate for use in multifunctional packaging films. A study incorporating SM into PCL found that the film greatly slowed browning of freshly cut apples and increased the oxygen scavenging, antioxidant, and antimicrobial capacities of films (Jeong et al., 2020). Antioxidant and antimicrobial peptides can also add various functions by joining the PCL polymer. For this purpose, a multilayered film was formed with PCL by encapsulating the antimicrobial palindromic peptide LfcinB (21-25) Pal into pullulan (PUL) electrofibres. PUL is a polysaccharide of microbial origin produced by *Aureobasidium pullulans*. The antimicrobial peptides used, by inhibiting the enzymatic activities of the cell walls of microorganisms and protein synthesis, disrupted the structural integrity and showed antimicrobial properties (Rodríguez-Sánchez et al., 2020; Rodríguez-Sánchez et al., 2023).

There are many types of mushrooms used for medicinal purposes in nature. Mushroom extracts can be used as polymer additives due to the dozens of substances they contain, such as proteins, peptides, fatty acids, nucleotides, steroids, sterols, phenolic compounds, terpenes, carbohydrates. In a study, *Ganoderma lucidum* extract was used as a mushroom variety to fortify PCL nanofibers. Modified PCL nanofibers increased the oxidative stability of rainbow trout fillets during storage (Nabati et al., 2023). Antimicrobial enzymes can also be used as bioactive substances in packaging. The glucose oxidase (GO) enzyme reacts with D-glucose units to produce hydrogen peroxide (H_2O_2), which damages the cell membrane. Films consisting of polyvinyl alcohol (PVOH) and double PCL membrane in which GO was immobilized inhibited *E. coli* bacteria (Alonso-González et al., 2020).

3. Conclusion

In this literature study, the food packaging applications of the modified PCL polymer in recent years are included. Today, studies on PCL have generally focused on strengthening the mechanical, gas barrier and thermal properties, which are the disadvantageous side of PCL, and functionalizing the polymer with various chemicals. These studies show us that PCL is a suitable alternative for producing packaging materials that do not harm the environment with its biodegradable nature and meet the requirements of the industry. While modifications to PCL can only be in the form of adding bioactive components, there are many studies in which many modifications are applied together. For this reason, an improvement can give the PCL film both structural and antimicrobial features. This versatile approach expands the usage areas of the polymer. Film production techniques developed in recent years have turned packaging films into sensors used for different purposes. This sensor-packaging approach opens new horizons, especially in preserving food quality and reducing the negative effects of microbial spoilage on shelf life. Since the chemicals used in modifying the PCL polymer should not pose a health threat, it is also important to obtain these chemicals from plant sources. Since plants are extremely rich in antimicrobial and antioxidant, these capacities are studied for functionalizing the films. In addition, many substances that are not harmful to human health, such as nanoclays, enzymes, peptides, acids, nanometals, and graphene are used in PCL modification. As the demand for biodegradable and functional polymers such as PCL will increase due to decreasing natural resources in the future, studies on PCL will gain more importance.

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