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Review

Trends and challenges in the development of bio-based barrier coating materials for paper/cardboard food packaging; *a review*

Muhammad Mujtaba [a,d,*], Juha Lipponen [a], Mari Ojanen [b], Sami Puttonen [b], Henri Vaittinen [c]

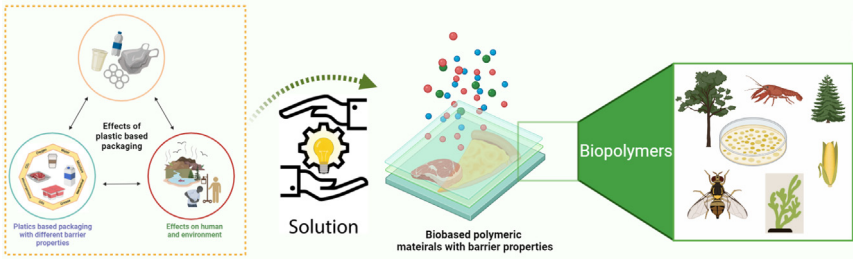
[a] *Aalto University, Bioproduct and Biosystems, 02150 Espoo, Finland*
[b] *Kemira Oyj, Energiakatu 4, 00101 Helsinki, Finland*
[c] *Valmet Technologies, Wärtsilänkatu 100, 04440 Järvenpää, Finland*
[d] *VTT Technical Research Centre of Finland Ltd, P.O. Box 1000, Espoo FI-02044, Finland*

HIGHLIGHTS

- Food packaging pays a key role in food safety and food quality.
- Fossil based barrier coatings are causing serious environmental and health problems.
- Biobased polymers can replace petroleum-based barrier ingredients.
- The barrier properties of bioplastics need to be enhanced to make it applicable on industrial scale.
- Cellulose, Chitosan, and bio polyesters are among the strong candidates for green packaging.

GRAPHICAL ABSTRACT

Biopolymers based coatings and films for packaging.



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ABSTRACT

Currently, petroleum-based synthetic plastics are used as a key barrier material in the paper-based packaging of several food and nonfood goods. This widespread usage of plastic as a barrier lining is not only harmful to human and marine health, but it is also polluting the ecosystem. Researchers and food manufacturers are focused on biobased alternatives because of its numerous advantages, including biodegradability, biocompatibility, non-toxicity, and structural flexibility. When used alone or in composites/multilayers, these biobased alternatives provide strong barrier qualities against grease, oxygen, microbes, air, and water. According to the most recent literature reports, biobased polymers for barrier coatings are having difficulty breaking into the business. Technological breakthroughs in the field of bioplastic production and application are rapidly evolving, proffering new options for academics and industry to collaborate and develop sustainable packaging solutions. Existing techniques, such as multilayer coating of nanocomposites, can be improved further by designing them in a more systematic manner to attain the best barrier qualities. Modified nanocellulose, lignin nanoparticles, and bio-polyester are among the most promising future candidates for nanocomposite-based packaging films with high barrier qualities. In this review, the state-of-art and research advancements made in biobased polymeric alternatives such as paper and board barrier coating are summarized. Finally, the existing limitations and potential future development prospects for these biobased polymers as barrier materials are reviewed.

Abbreviations: AM, amylose; AP, amylopectin; CA, cinnamic acid; CSE, cellulose stearoyl ester; CNF, cellulose nanofibers; LNPs, lignin nanoparticles; OTR, oxygen transmission rate; PA, polyamide; PET, polyethylene terephthalate; PE, polyethylene; PHA, polyhydroxyalkanoates; PDMS, polydimethylsiloxane; PLA, polylactic acid; PVC, polyvinyl chloride; PP, polypropylene; PVOH, poly (vinyl alcohol); WCA, water contact angle; TOFA, Tall oil fatty acid; WVP, water vapor permeability; WVTR, water vapor transmission rate.

* Corresponding author at: VTT Technical Research Centre of Finland Ltd, P.O. Box 1000, Espoo FI-02044, Finland.
E-mail address: muhammad.mujtaba@vtt.fi (M. Mujtaba).

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Contents

1. Introduction

Packaging plays a key role in a product's safety from the external environment. In other words, the packaging material must contain excellent barrier properties against the transport of different permeants such as moisture, gases, and lipids across the packaging wall (Cheng et al., 2022; Weligama Thuppahige and Karim, 2022). The major ingredients used in cardboard/paper packaging materials to introduce the barrier properties are based on plastics (Ong et al., 2022), glass (De Feo et al., 2022), and metals. Currently, the annual global production of plastics has crossed the value of 320 million tons (Luzi et al., 2019; Paletta et al., 2019). With the increasing prices of fossil fuels, the plastic industry is using polymers such as polyvinylchloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), polyethylene (PE), and polyamide (PA) (Jain and Tiwari, 2015; Luzi et al., 2019). However, the use of such non-renewable and non-degradable materials not only causes a potential health risk but also emits greenhouse gases such as CO_2 and methane, leading to major environmental risks (Bohlmann, 2004; Shen et al., 2020). Additionally, the application of plastics, glass, or metal-based ingredients as barrier lining in paper-based packaging containers makes the recycling process challenging, increasing the overall recycling costs. Switching from petroleum-based plastics to sustainable polymers has emerged as the most practical substitute to decrease the environmental pollution caused by non-degradable packaging materials. In this regard, the quest for biobased alternative materials is thriving day by day to replace the existing petroleum and metal-based ingredients in the packaging industry (Chausali et al., 2022; Nilsen-Nygaard et al., 2021).

Biopolymers are gaining popularity in the packaging business due to their numerous benefits such as biodegradability, non-toxicity, and biocompatibility (Reichert et al., 2020). These biopolymers include polysaccharides (chitin, chitosan, cellulose, starch, alginate, and alpha glucans), lipids (bee waxes, free fatty acids), and proteins (Fig. 1) (Liu et al., 2021; Moeini et al., 2021). Biobased polymers offer excellent barrier properties (moisture, gas, thermal, and grease), when applied under optimal manufacturing conditions and concentrations. Several researchers have so far demonstrated the use of biobased polymers to improve the barrier qualities of packaging materials (Moeini et al., 2021). These biopolymers have been applied in different forms such as coating, bio-nano composites, and blend films (Fernández-Marín et al., 2021; LakshmiBalasubramaniam et al., 2022; Mujtaba et al., 2021; Tarique et al., 2021). Besides the enormous advantages offered by biopolymers, numerous physical and chemical properties such as high molecular weight, hydrophilicity, crystallization, aggregation, brittleness, and weak mechanical properties need to be improved as they are considered major constrain in the industrial-scale application of these polymers (Mujtaba et al., 2019).

Among these biopolymers, cellulose (nanocrystals, nanofibers, and nanofibrils), chitosan, alginate, lignin, modified starches, and bio-polyesters have successfully attracted the interest of researchers as well as paper industries (Rastogi and Samyn, 2015). This widespread interest is due to the excellent properties offered by biopolymers i.e., renewable sources (forests and some marines), high surface area and aspect ratio, barrier properties, nontoxicity, biodegradability, and biocompatibility (Brodin et al., 2014; Kjellgren et al., 2006; Rastogi and Samyn, 2015; Rhim et al., 2006). The above-mentioned properties enable biobased polymers to find their place in different applications ranging from cosmetics, food, paints, biomedicine, tissue engineering, and pharmaceuticals. Numerous reports have suggested some prominent results of different polymers such as cellulose nanocrystals, chitosan, bio-polyesters, modified starches, lignin and alginate as coating materials for enhancing the barrier properties of paper/cardboard (Chi et al., 2020; Tyagi et al., 2021).

Although several review articles (Basavegowda and Baek, 2021; Basumatary et al., 2022; Khalid and Arif, 2022; Kumar et al., 2022; Taherimehr et al., 2021) are present describing the recent advances in biopolymers for different applications including barrier enhancement, however, the number of articles discussing the current trends and challenges in designing and applications of biopolymers as a barrier enhancing coating materials for cardboard and paper-based substrates is very scarce. This review will cover challenges and recent developments in the identification, production, and application of biopolymeric barrier materials especially cellulose, lignin, chitosan, starch, alginate, PHA, and polylactic acid (PLA) for packaging (films and paper coating). Besides, a brief future perspective section will also be provided.

2. Approach and scope

The scope of this article is limited to the current trends and challenges associated with the development and application of biobased coatings/films for paper and cardboard-based packaging systems to enhance their barrier properties. Before digging deep into the current trends in literature, the

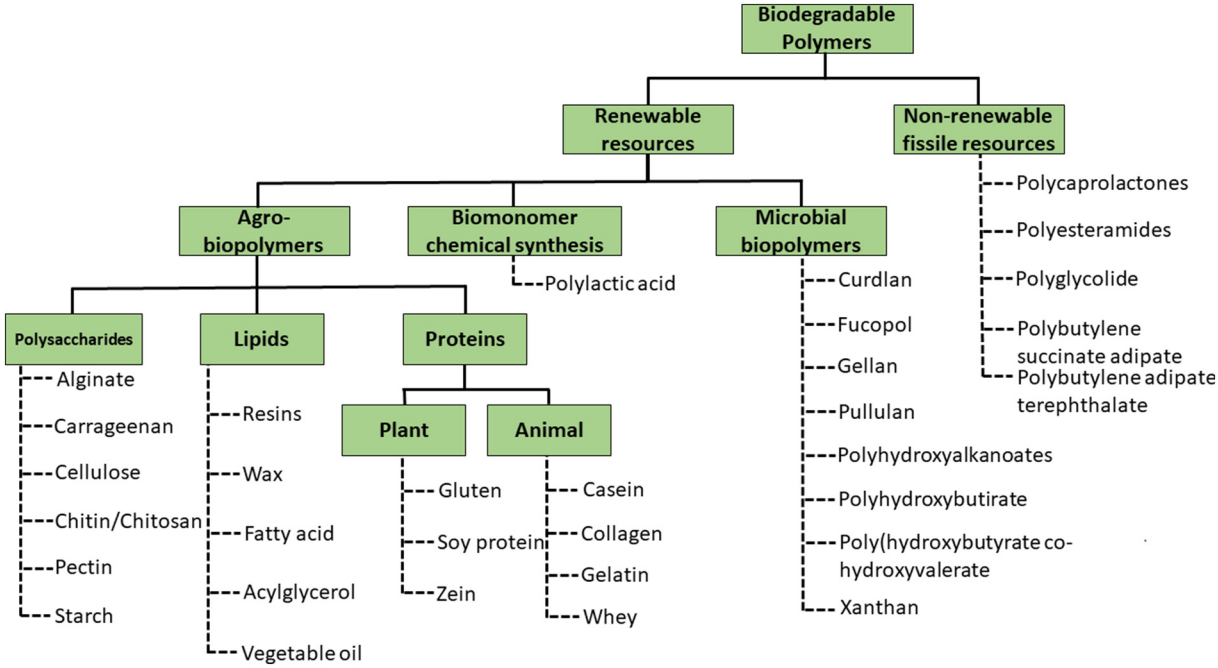

Fig. 1. Classification of biodegradable polymers.

comprehensive theoretical background of vital barrier properties aided by current literature examples has been provided. The data on current advancements and challenges in biobased coatings and films for paper and cardboard application is extracted around mid of February 2022 from the Web of Science (WOS) Core Collection with a time span set as 2008 to 2022. Besides, "barrier coatings cardboard", "cellulose as barrier coating", "chitosan barrier coatings for packaging", "alginate coatings and films", "lignin barrier coating applications", "modified starch as barrier coating", "biopolymer-based coatings for paper and cardboard", "bio-polyesters based coating solutions for barrier coatings", etc. English was used as a set language and all document types were selected during this literature analysis.

3. Concepts of barriers in food packaging

Packaging material is known to significantly contribute to the qualitative parameters of food products such as taste, smell, longevity, and marketability. A considerable amount of food spoils every year across the globe (around 40 % only in the USA) due to technical limitations of packaging (Gunders, 2012; Restuccia et al., 2010).

Barrier properties of a material can be defined as; the protection of food commodities inside the package by preventing the entry/exit of different penetrants such as moisture (water vapors), oxygen, carbon dioxide, greases, and oils (Fig. 2) (Sangroniz et al., 2019). Packaging material needs to resist the permeation of water, oxygen, grease, micro-organisms, aromatic compounds, carbon dioxide, and oils (Lange and Wyser, 2003; Sangroniz et al., 2019). The paper/cardboard-based packaging exhibits weaker barrier properties and is permeable to gases, water vapors, and liquids (Khwaldia et al., 2010). On the contrary, plastic-based packaging offers a wide-ranging mass transfer characteristic that ranges from low to excellent barrier value (which is of vital importance when it comes to food packaging) (Beitzen-Heineke et al., 2017). Synthetic polymers such as polyethylene (PE), polypropylene (PP), and ethylene vinyl alcohol (EVOH) have been widely used to improve the overall barrier attributes of paper-based packaging (Maes et al., 2018; Tyagi et al., 2021). For

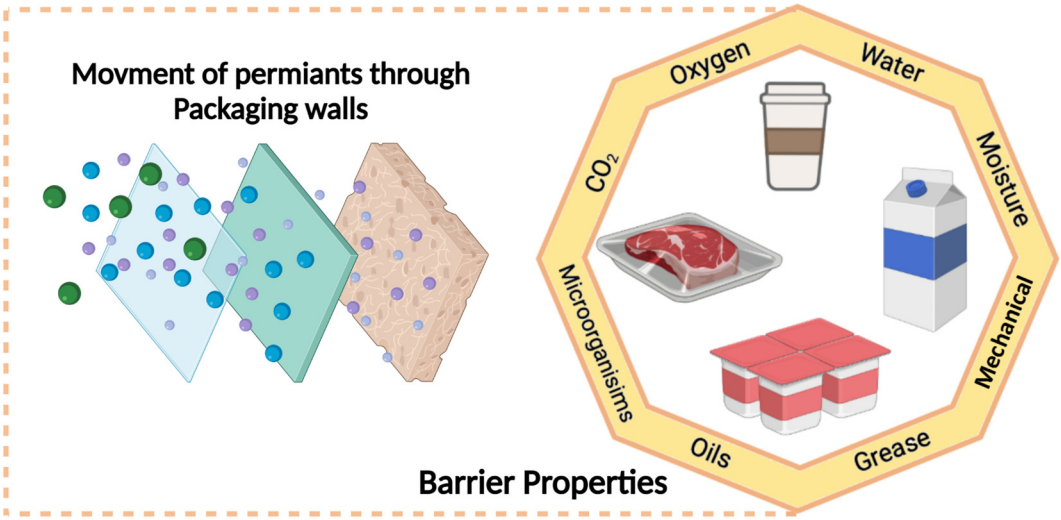

Fig. 2. Different barrier properties of packaging material.

example, coffee cups and cotton board boxes for burgers have been incorporated with an inner laminating layer of such synthetic polymers (Tyagi et al., 2021).

However, the use of these petroleum-based polymers in cardboard board/paper packaging is causing considerable environmental and economic concerns. The complete recycling process of cardboard packaging with an inner plastic lamination is challenging, as plastics are not water-soluble. This makes the recycling process more uneconomical and affects the overall circle of a sustainable/circular economy (Kaiser et al., 2017). To cope with this situation, researchers from divergent fields of science and industries are striving for a biobased alternative to replace these petroleum-based laminations in paperboard packaging. This review will focus on the use of biopolymers as coating material for paper-based packaging to enhance its barrier properties.

Barrier properties of a polymeric material candidate for packaging application play a vital role in predicting its potential to protect the product. These barrier properties strongly depend upon the specification of a product and end-use applications (Sangroniz et al., 2019). The barrier properties of a packaging material (film, paperboard) are influenced by the thickness and crystallinity of the paper material, size, and polarity of the permeant (Wang et al., 2018b). The transmission of permeants is influenced by storage conditions i.e., humidity and temperature. The entry or exit of permeants is highly dependent upon the cohesive energies between the barrier wall and molecule. In the case of higher permeation, the overall cohesive energies between the barrier wall and molecules are at the lowest value, whereas the non-permeant molecules indicate higher cohesive energies (Auvinen et al., 2008; Riley, 2012). Water vapor and oxygen are termed as two major permeants as they can be easily transferred from the external environment by crossing the polymeric wall and affecting the quality of the food product (Arora and Padua, 2010).

3.1. Water barrier/super hydrophobic surfaces

Glass, metal, and plastics are among the commonly used packaging materials for different types of food commodities such as dairy beverages, fresh vegetables, meat, ready to go food, juices, and water. These materials have been used as they offer a good barrier against water and other permeants. However, the extensive use of these conventional packaging materials is reflected in increased transportation and recycling costs (Verma et al., 2021). Besides, they are also posing environmental concerns due to their non-decomposition in landfills. Biobased polymers have appeared as a promising alternative to petroleum-based plastics. For the past few decades, different types of biopolymers i.e., PLA, cellulose, chitosan, alginate, starch, zein, whey protein, PHA, etc., have been tested in food packaging applications (coating, films, composites, etc.) (Rastogi and Samyn, 2015).

Considering the up-to-date literature, research has been diverted towards the improvement of various barrier properties of these biopolymers so that they can compete with petroleum-based polymers such as PET (polyethylene terephthalate), ethylene vinyl alcohol (EVOH), polyvinylidene chloride (PVDC), nylon and polycarbonate, etc. (Kansal et al., 2020a; Kraśniewska et al., 2020; Lionetto and Esposito Corcione, 2021).

Among other barrier properties, the water barrier is considered an important barrier feature that is related to the end-use application of the material. For liquid beverages with higher water contents, the development of a highly hydrophobic surface is essential to sustain the packaging material and prevent deterioration. For example, the packaging of milk products consists of PET (highly hydrophobic >150°) lining water barrier, aluminum lining as gas and UV-light barrier, and carton boards for structure and printability (Fotie et al., 2020). To replace the PE lining (a petroleum-based plastic), biobased polymers such as cellulose, starch, and alginate have been considered (Platnieks et al., 2020; Triantafillopoulos and Koukoulas, 2020). However, the main problem that needs to be dealt with before using such biopolymers is their higher hydrophilicity. The hydrophilic nature of polysaccharide-based polymers (cellulose, chitosan, starch, etc.) comes from the OH groups that are present along the backbone of polymeric chains (Mujtaba et al., 2019).

Interest is increasing in the development of super hydrophobic surfaces that can be utilized in the packaging of food products i.e., especially dairy products and beverages. Super-hydrophobic surfaces are classified as surfaces with a contact angle >150° and a sliding angle of approx. 10° (Barati Darband et al., 2020; Parvate et al., 2020). Surface chemistry and physiology both affect the overall hydrophobicity level of the material (Li et al., 2019a). The basic concept of hydrophobicity can be well-defined by young's equation. According to Young's equation, the contact angle of a liquid is related to the interfacial energies between solid-liquid, solid-vapor, and liquid-vapor (Young, 1805). The equation has been described as;

$$\mathrm{Cos}\theta^{Y} = \sigma_{SV} - \sigma_{SL}/\sigma_{LV} \tag{1}$$

Here ^{Y} denotes the name of Thomas Young and contact angle of an ideal system smooth surface with respect to a liquid. $\sigma_{SV,}$ σ_{S}, σ_{LV} denotes surface tension for a solid in equilibrium with solid vapor, solid–liquid, and liquid vapor respectively.

The highest contact angle for a certain surface can be achieved with the lowest surface energy. So far, fluorine-containing surfaces such as CF_2-CF_2H and CF_3 have been reported with the lowest surface energies due to the strong bond between C and F (Song and Rojas, 2013). On the other hand, naturally, existing hydrophobic surfaces such as lotus leaves and rose petals show higher contact angle values than those produced synthetically. The reason behind this high contact angle of natural surfaces lies in the morphologic attributes known as the roughness of the given surface (Zhang et al., 2017). Natural surfaces are rarely completely smooth as they have micro or nano roughness.

So far, numerous articles have reported different tools and strategies to introduce hydrophobicity to different substrates for different applications, especially carton board and paper for the development of sustainable packaging alternatives (Table 1) (Wang et al., 2022; Xu et al., 2021b). The chemical modification of substrate having smooth surfaces enhances the contact angle up to approx., 110–120°. For this purpose, different compounds with low surface energies have been applied in the form of coating or spray (Chen et al., 2022). However, raising the contact angle values to a super hydrophobic state (above 150°) requires the presence of micro and nano scale roughness on the surface (Tang et al., 2011). The role of micro and nano roughness has been better explained by Wenzel and Cassier-Bexter equations (Cassie and Baxter, 1944; Wenzel, 1936). Different approaches have been adopted to introduce micro and nano-scale roughness on different substrates, especially cellulose and similar polymeric based substrates (Table 1).

3.2. Grease/oil

Oleophilic surfaces are surfaces having more affinity towards oil/grease than water. The oil wetting phenomena in oleophilic carton boards display similarities with hydrophobicity/hydrophilicity phenomena. Oil permeation to the carton board surface usually takes place by capillary flow through pores or cavities (Andersson et al., 2002; Roberts, 2004). The flow of fluids through the capillary can be quantified by using the Lucas-Washburn equation. Lucas-Washburn equation quantifies the fluid permeating through the pores of cardboard. According to the Lucas-Washburn equation (Washburn, 1921), the penetration rate of a fluid through a cardboard substrate is;

$$\frac{dh}{dt} = \frac{r\gamma cos\theta}{4\eta h}$$

Here h denotes the total distance traveled by fluid in time t, and r represents the radius of the capillary. γ is the surface tension' θ is the angle of liquid with a capillary wall and η is the viscosity of a fluid.

Table 1
Approaches for introducing super hydrophobicity in different polymeric materials.

Modification approach	Polymers	Water contact angle (WCA)	References
Chemical Etching	Cellulose nanocomposites	>150°	(Gonçalves et al., 2008)
Plasma etching	Lignocellulosic wood fibers and mineral fillers (calcium carbonate, talc, or clay)	>152°–162°	(Mirvakili et al., 2013)
Photo lithography	UV-curable polyurethane functionalized with acrylate groups	>159°	(Lee et al., 2014)
Nanosphere lithography	Chitosan	>152°	(Jung et al., 2019)
Fiber electrospinning	Cellulose triacetate fibrous mats, cellulose nanofibers	>153°	(Dizge et al., 2019; Yoon et al., 2009)
Chemical vapor deposition (CVD)	Superhydrophobic polytetrafluoroethylene (PTFE) films	>150°	(Zhuang et al., 2017)
Sol-gel coatings	Cellulose membrane	>159°	(Xie et al., 2019)
Nanoparticle spray coating	Chitosan–silica	>150° to 159°	(Liu et al., 2016)
	Tailor-modified lignocellulose nanofibrils	>160°	(Zhong et al., 2019)
	Chitosan-based coatings	>140°–157°	(Ivanova and Philipchenko, 2012)
Solution-immersion	Cotton fabric or paper	>157°	(Li et al., 2008)

The paper contains inherent voids and pores that facilitate the absorption of oils and grease through capillary force (Brown, 2004). Besides, the oleophilic nature of cellulose further adds to the oil absorption property of paper, diminishing the effective use of paper-based packaging. Numerous approaches have been investigated to enhance the grease barrier properties of paper-based packaging materials (Li and Rabnawaz, 2018; Nowacka et al., 2018). These include polymeric coating of substrates with low-energy chemicals such as fluorine, application of laminating agents, and etching of substrate surface for micro and nanoscale roughness. The highly refined pulp can also contribute to the grease barrier (e.g., baking papers, MFC) (Lu et al., 2016).

3.3. Oxygen permeability

Excessive oxygen permeability through a packaging material accelerates the deterioration and consequently reduction of shelf life of food commodities. An oil rich food commodity in an O_2 permeable package changes color and taste due to lipid oxidation (Moyssiadi et al., 2004). Besides, O_2 permeability leads to extensive microbial growth inside the package that causes product spoilage (Taherimehr et al., 2021). Therefore, the development of materials with excellent barrier properties to regulate the transport of O_2 across the packaging wall is among the burning research topics for food industries and researchers. Packaging materials showing good O_2 barrier properties can warrant both economic loss (due to reduced product quality) and danger to human health (due to microbial spoilage). For this purpose, different approaches such as blending different polymers (Ilyas et al., 2022), multi-layer coatings (Chang et al., 2021), crosslinked polymers (Sheng et al., 2021), nanocomposites with nanoparticles (Phothisarattana et al., 2022), nanosheets (Xu et al., 2021a), microcrystals (Paul et al., 2021), nanofibers (Sánchez-Gutiérrez et al., 2021), etc., have been tested to design packaging materials with high oxygen barrier properties. Before stepping into the details of each approach this section will describe the basic mechanisms and principles of oxygen mass transport.

The rate of oxygen transmission through a substrate is expressed as cubic centimeters of oxygen that pass through an m^2 of a substrate in the presence of oxygen pressure 1 atm greater than that on the other side of the packaging for 24 h, at a specified temperature (Baele et al., 2021). The oxygen transmission rate can be calculated by using the following equation.

$$\Delta mgas/\Delta t = P\,A\Delta p/\Delta p \tag{2}$$

Here $\Delta mgas/\Delta t$ stands for the transmission rate of oxygen, P denotes the permeability of packaging material and A denotes the contact area of packaging material, Δp is the partial difference in pressure across the packaging material, L is the thickness of the material.

Several factors have been determined that affect the rate of oxygen permeability through a packaging material. This set of factors can be divided into two major categories: i.e., properties of polymers/biopolymers and environmental effects (Siracusa, 2012). The chemical and physical structure of packaging materials plays a critical role in defining the oxygen barrier property. The affinity of oxygen molecules towards the polymeric structure of the matrix affects the rate of oxygen mass transfer through the package wall. Similarly, the ratio of crystalline and amorphous structure of substrate affects the transport of oxygen molecules. Other polymeric attributes that affect the permeability of oxygen and OTR includes, a) the presence and lengths of pedant chains. Pedant chains with higher lengths affect the crystallinity of the polymer. Longer side chains contribute to a more rigid polymeric structure that leads to restricted chain mobility. Therefore, the free volume increases in the polymeric structure and accordingly enhances oxygen permeability (Ghasemnejad-Afshar et al., 2020). b) the ratio of crystalline and amorphous regions in polymer also influences the rate of oxygen permeability (Idris et al., 2021). As is known that in amorphous regions the polymeric chains align irregularly without any proper geometrical arrangement. This leads to the creation of more free volumes and less density in the structure, leading to enhanced oxygen permeability. On the other hand, in the case of crystalline regions, the polymer chains align more regularly and periodically. This arrangement increases the density of polymer resulting in reduced oxygen permeability through the packaging material. c) the formulation of the polymeric matrix is also among the defining factors of the oxygen transmission rate (Idris et al., 2021).

Currently, polysaccharides are used to enhance various barrier properties of the packaging materials. However, the use of certain polysaccharides in the matrix enhances the oxygen transmission rate. This can be ascribed to the fact that the application of polysaccharides requires plasticizing agents such as glycerol and sorbitol. The use of these plasticizers increases the OTR as they interfere with the overall crystallinity of the matrix (Miller et al., 2021). d) the processing of polymers also plays an important role in enhancing the barrier properties of a polymeric matrix. Processes involving the enhancement of crosslinking and crystallinity are highly desired. e) physical and chemical interaction between penetrant and barrier material is also among the crucial factors. This includes the chemical (presence of functional groups or bonding sites for penetrant) and physical (morphology and polymeric structure) properties of penetrant and matrix. f) temperature and humidity are among the environmental factors that contribute to the increase or decrease in OTR (Reinas et al., 2016).

3.4. MAP (modified atmosphere packaging)

Modified atmosphere packaging has a prominent place in the food industry. Historically, the terms modified atmosphere or controlled atmosphere were used for packaging containers, and storage deposits with different levels of oxygen, carbon dioxide, and ethylene (Floros, 1990). This process has been used by older civilizations like Greece and China. Early records reported storing fruits together with fresh leaves in sealed clay containers. It was believed that the presence of fresh leaves and grass inside the container speeds up the overall ripening process of fruits by creating an internal environment with low oxygen and high CO_2 (Church and Parsons, 1995). However, until 1820 no scientific study was conducted to investigate the effect of these gases in a modified atmosphere on fruit ripening. Scientific evidence was provided after 100 years when by studying the effects of CO_2 and O_2 on the growth of fruit-rotting fungi in 1920. Following

this report, several studies were published reporting the effect of CO_2, O_2, and other gases on the fruit ripening process (Floros and Matsos, 2005). In MAP packaging systems, the inner atmosphere is kept by either active or passive means. In the case of active means, the final concentration and change rate of gases depends upon the packaging material and product inside (Czerwiński et al., 2021). For example, fresh products like vegetables and fruits continue to live after harvesting by consuming oxygen from the surrounding environment. In case of atmospheric alteration through passive means, the concentration of essential gases is altered inside the packaging container due to the product. This product-linked gas alteration inside the packaging container occurs due to oxygen consumption by the microflora of a product and biochemical and physiological processes (Falagán and Terry, 2018). In the case of passive MAP, the attainment of the desired atmosphere is a slower process compared to active MAP (Paulsen et al., 2019).

MAP packaging systems are used for the extension of shelf life by inhibiting the microbial growth inside the package, preventing product structural deterioration by reducing the undesirable biochemical and physiological events, sensory attributes, and overall nutritive value by preventing contamination (Fig. 3). In MAP, a mixture of CO_2, and N_2 is used to prevent the microbial growth and enhance the shelf life. N2 is introduced to MAP to replace the oxygen inside the package leading to a reduction in rancidity and microorganisms' growth. However, minting the required levels of residual oxygen inside a MAP is the main concern for food processors. For example, highly oxygen-sensitive food commodities require 1–2 % of residual oxygen, while in the case of dry food items such as nuts this value goes up to 2–4 %. Sustaining different levels of oxygen for different products is enormously vital and highly dependent upon the applied oxygen barrier material inside the MAP. The barrier properties of plastic-based MAP can be easily impaired by various factors such as moisture, aromatic compounds, and fluctuations in temperature. The adsorption of food material by plastic-based MAP walls can lead to the deterioration of the oxygen barrier through adhesion between the multi-layer packaging system. Willige et al. (2002) reported a significant linear increase in oxygen permeability of low-density polyethylene (21 %) and poly propylene (130 %) based packaging following an 8-hour exposure to aromatic compounds.

Biopolymers-based oxygen barriers are emerging as a green, resistant, and tunable alternative to plastics in MAPs. TEMPO-oxidized (2,2,6,6-tetramethylpiperidine-1-oxyl–mediated oxidation) CNFs were applied as multilayer coating on MAP pouches. The oxygen transmission rate was decreased from 2100 ± 200 $cm^3\ m^{-2}$-day (single coating layer) bar to 400 ± 100 $cm^3\ m^{-2}$ day bar (three layers of CNF coating) at 80 % relative humidity (Vähä-Nissi et al., 2017). In another similar study, Syverud and Stenius (2009) prepared CNF films as candidate barrier materials for MAP and reported the OTR values as 17.75 ± 0.75 $cm^3\ m^{-2}\ day^{-1}$ at 23 °C and 0 % of relative humidity (RH). Latou et al. (2014) treated MAP bags with chitosan as a barrier coating material. Chitosan-treated samples successfully maintain CO^2 concentration higher enough (48.4 %) to exert the antimicrobial effect on tested chicken meat. Similarly, MAP samples (0 % CO_2/35 % N_2/5% O_2) were coated with locust bean gum-sodium alginate solution for enhancing the shelf life of Turbot (*Scophthalmus maximus*) under refrigerated conditions (Cao et al., 2021). As per results, coated samples revealed a significant reduction in oxygen and nitrogen concentration, bacterial growth, and spoilage. Micro-perforated poly-lactic acid (PLA) films were tested as potential equilibrium modified atmospheric packaging systems using cherry tomatoes and peaches as a model food commodity. Laser-perforated PLA films with different dimensions of perforations displayed good barrier properties to gases and water as required by the specific food sample.

3.5. Aroma

Food packages are expected to keep the quality of a food commodity for as long as possible during its storage. The sorption rate of gases and volatile compounds through packaging material dictates the shelf life of a product. Several food constituents come together to make the aroma of a food product. The permeation of these volatile aroma compounds through the packaging wall is a decisive factor in the organoleptic quality of food (Chaliha et al., 2013; Miller and Krochta, 1997). Considering these factors, researchers are designing packaging materials that can minimize the loss of these volatile aroma compounds. Among them, polyethylene and polypropylene-based surfaces have displayed excellent barriers against aroma loss due to their surface inertness (Dombre et al., 2015;

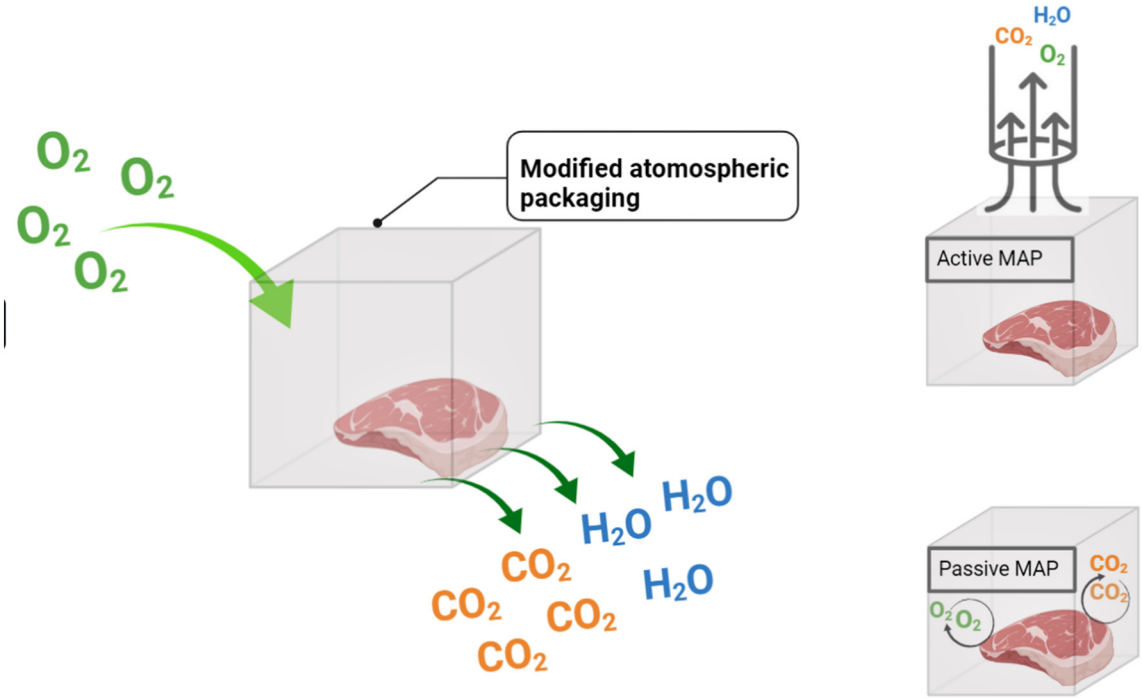

Fig. 3. Demonstration of modified atmospheric packaging; active MAP and passive MAP.

Leelaphiwat et al., 2018). The sorption of aromatic compounds is influenced by molecular size, total solubility, and polarity of aromatic compounds. Besides, polymer structure and properties also play a significant role in the permeation of these aromatic compounds. As is known, most of the aroma constituents are nonpolar, therefore designing packaging materials with polar surface features can make an excellent barrier to preventing loss of aroma (Wicochea-Rodríguez et al., 2019). The crystallinity of the applied polymer also affects the aroma permeability. The crystalline regions of a polymeric matrix are hard to permeate for aroma constituents (Miller and Krochta, 1997). So far there is no standard quantification method for measuring the transport of aromatic compounds across the package wall. However, researchers are using different alternative methods for this purpose, i.e., contact between polymer and diluted vapor of aromatic compounds, contact between polymer and aqueous solution of aromatic compound etc. (Vähä-Nissi et al., 2008). Besides, the permeation analysis is made using saturated vapor of the aroma compound. Diffusion coefficient is decided from permeation or sorption kinetics.

Biopolymers or biodegradable-based packaging materials offer an excellent barrier against aroma permeability (Miller and Krochta, 1997). Cherpinski et al. (2018b) reported the use of annealed electrospun ultrathin fibers from poly(3-hydroxybutyrate), poly (vinyl alcohol), and polylactide as a paper coating for enhancement of barrier properties. As per the results, PHB-based multilayered electrospun fiber structures revealed higher aroma barrier properties compared to PLA-based structures. The aroma barrier is highly dependent on the thickness of the coated film and in the case of PHB fibers, electrospun fibers yield film with higher thickness compared to PLA films. Similarly, PVOH-based electrospun fiber film did not contribute to the enhancement of the aroma barrier. This was ascribed to two factors, a) film thickness and b) moisture content of PVOH (Cherpinski et al., 2018b). It has been reported that in a dry state PVOH exhibits a good affinity towards organic vapors. However, in most cases due to the use of plasticizing agents, PVOH contains residual moisture, that decreases its affinity towards aromatic compounds. Similarly, whey proteins present excellent barrier properties against aromas and oil (Krochta, 2002). In a similar study, a multilayer coating of alginate and chitosan was applied to paper-based packaging. In alginate-coated paper samples, the migration of mineral aromatic hydrocarbons was decreased from 6.02 ± 0.16 % to 2.41 ± 0.42. While in the case of chitosan, the migration of aromatic hydrocarbons decreased from 6.02 ± 0.16 % to 0.73 ± 0.34. The better performance of chitosan can be ascribed to the overall film thickness and affinity of polymer to aromatic hydrocarbons (Kopacic et al., 2018).

3.6. Heat isolation

Temperature is also one of the crucial factors affecting the quality of food commodities. Packaging systems are expected to control the inside temperature to the best level as per product requirements (Kim et al., 2014). Heat entrapment by a packaging system occurred through conduction (transfer of kinetic energy from one molecule to another), convection (transfer of heat through physical means), and radiation (heat transfer through electromagnetic waves). The insulating ability of packaging material is influenced by wall thickness, number of reflective layers, and number of other surfaces (Choi, 2006). Currently, the materials that are in service as heat insulators inside a packaging system include expanded polystyrene, polypropylene, polyurethane, aluminum foil, corrugated cardboard, etc. (Song et al., 2014). These materials use low thermal conductivity as a tool for restricting heat transfer. Highly reflective materials such as aluminum foils are used for preventing heat transfer through radiation. Fibers, foams, loose-fills, and reflectors used by the packaging industry rely on their low density and entrapped air for slowing down the heat transfer across the wall (Lange and Wyser, 2003).

With the current advancements in polymer science and nanotechnology, polysaccharides are becoming potential key players in the field of insulating materials for food packaging (Singh et al., 2008). Among other biopolymers, polysaccharides draw attention, thanks to their excellent film and gel-forming ability. Hydrogels and aerogels dried through supercritical CO_2 drying rout can offer excellent thermal insulating properties (Smirnova and Gurikov, 2017). Numerous studies have reported the production of polysaccharide-based aerogel providing thermal conductivity lower than air (~26 mW m^{-1} K^{-1} at 300 K), which can be applied as a thermal insulation barrier layer in food packaging. Porosity and suitable drying conditions mainly define the thermal conductivity of hydrogels, aerogels and alcogels. Methods like freeze drying involve the removal of water through a process called sublimation. However, besides the removal of water, freeze drying cause expansion and distortion of polymeric chain networks affecting the porosity of hydrogels (Nešić et al., 2018). Distortion and expansion of polymeric chains lead to irregular pore structures and consequently high polymer density and lower thermal insulating properties. Gurikov et al. (2015) reported a novel gelation approach to produce alginate-calcium carbonate aerogels with micro-*meso* porous surface morphology. The thermal conductivity of the alginate aerogel samples (mesopore volume 6.98 cm^3 g^{-1}) dried with supercritical CO_2 was recorded in the range of (18–22) ± 2 mW m^{-1} K^{-1} significantly lower than the conductivity of free air. In a similar report by Rudaz et al. (2014) reported the preparation of monolithic pectin aerogels, and aeropectin by using a dissolution-gelation-coagulation approach followed by drying through supercritical CO_2. Aeropectin with both micro and mesopores revealed thermal conductivity in the range of 16–22 mW m^{-1} K^{-1}. This kind of biobased thermal super insulating material can open new opportunities in the development of biomass based thermal insulators for packaging systems.

3.7. UV-light barrier/antioxidant

The exposure of food products to natural and artificial light (UV (100–400 nm) and visible light (400–700 nm) and near-infrared range (700–2200 nm)) is probable during distribution, packaging, and consumption. Although around 3 % of UV radiation reaches earth, it is still causing chemical reactions, weathering of polymers, and fading of certain colors. Therefore, UV barrier blocking is an important property in bio/polymers that are supposed to be adopted in multiscale applications. The exposure of food products to UV and visible light results in several harmful effects such as the degradation (photo) of proteins, fats and oil, vitamins, and pigments (Cassar et al., 2020). Photooxidation or photodegradation of food products caused due to the presence of photosensitizers present in food. These photo-synthesizers are the constituents of food that are light-sensitive and absorb light upon contact. In the presence of light and oxygen photo-synthesizers initiate the process called photosensitization. In photosensitization, photons from the light break down the bonds between the photo-synthesizers (Kwon et al., 2018). Reactive oxygen species ((oxygen radicals such as superoxide anion, hydroxyl, peroxy, alkoxy, and hydroperoxyl radical) and nonradical derivatives (i.e., hydrogen peroxide, ozone, and singlet oxygen)) are generated by the process of photosensitization. ROS (Reactive Oxygen Species) affects the quality of the product causing undesirable chemical alteration in food ingredients, off-flavors, reduction in nutritive quality, and color change. Products like milk, dairy items, meat, vegetable oils, and wine are mostly affected by photosensitizers as they are rich in fatty acids and proteins (Kwon et al., 2018).

To prevent photodegradation via photosensitizers, the packaging industry has adopted various technologies including, reflective layers, coating with organic and inorganic absorbers, etc. Inorganic light absorbers include titanium dioxide (TiO_2), zinc oxide (ZnO_2), cerium oxide (CeO_2), iron oxide (FeO_2), etc. (Shirsat et al., n.d.). Organic light-absorbing materials include phenolic-type absorbers hydroxyl benzophenones, hydroxyl flavones, xanthones, salicylates, hydroxyphenyl benzotriazoles, and hydroxyphenyl triazines (Kwon et al., 2018).

Biopolymeric (natural and synthetic) materials emerged as an approach to enhance the UV barrier resistance property of biobased packaging systems. Polymers like PLA (Shankar et al., 2018), PHBV (Sanchez-Garcia and Lagaron, 2010), PCL (Garcia-Garcia et al., 2018), lignin nanoparticles (Xing et al., 2019), clay MMT (Shikinaka et al., 2021), Furans (Furfural and 5-hydroxymethylfurfural) (Ahmed et al., 2021a), etc., have been analyzed for their UV barrier properties. Nano-clays exhibit UV barrier

Table 2
Effects of chitosan as a coating material alone or in combination with other polymers, proteins, and lipids on different barrier properties.

Polymer matrix	Coating methodology	Properties enhanced		Important outcomes	Reference
		Water vapor transmission and oil grease resistance	*Contact angle and air permeation*		
Nanocellulose/chitosan/carboxymethyl cellulose polyelectrolyte complexes (5, 10, and 20 %)	Wet coatings in water applied through dip coating approach.	WVTR decrease from 13,220 to 7982 g mm/m^2/d^1 KIT reduced from 12 to 8	Not described	Uniform coatings were obtained. With 5 wt% CNC content and good barrier properties were obtained.	(Chi and Catchmark, 2018)
Curdlan/chitosan	Chitosan-curdlan solutions were applied using an automated coater (5 g/m^2).	From 3.29 % to 4.04 %	Not described	Paper samples coated with blend of curdlan-chitosan resulted good barrier properties against water. Besides, for the same samples, the mechanical properties were significantly improved.	(Brodnjak, 2017)
Chitosan films with different concentrations of acorn starch-eugenol	1.5 % w/v chitosan dissolved in 1 % acetic acid and casted in Petri dish	From 2.648 ± 0.136 to 1.288 ± 0.321 (10^{-10} g/Pa·m·h)	75° ± 0.92 to 89° ± 0.98	Using starch and eugenol significantly improved the barrier, hydrophobicity, and antimicrobial and antioxidant properties of chitosan films.	(Zheng et al., 2019)
Chitosan with gelatin and phenolic extracts of grape seed and jaboticaba peel	1 % w/w chitosan solution in acetic acid incorporated with gelatin (2, and 2.5 g/g of chitosan) and extracts at different concentrations.	Decreased from 0.496 ± 0.076 to 0.049 ± 0.006 (g mm kPa^{-1} h^{-1} m^{-2})	56.24° ± 6.98 to 81.03° ± 3.71	The incorporation of seed extract and peel extract enhances the antioxidant, hydrophobicity, and WVP properties. The sequence of addition of the extract to the chitosan-gelatin mixture also has some effect on these properties.	(Rodrigues et al., 2020)
Chitosan crosslinked with genipin	1.2 wt% chitosan solution in 1.2 wt% acetic acid with genipin (in ethanol) was applied on paper using blade coater (Mayer bar; 6.46 cm/s and 300 g load.)	Decreased from 320 g/m^2·day to 155 g/m^2·day	78°-83° 47.4 to 21.3 mm^3·m^{-2} Pa^{-1} s^{-1}	The mixture of chitosan and genipin decreased air and water permeability. Good adhesion was obtained for cardboard compared to calendar paper.	(Oliveira et al., 2020)
Chitosan – palmitic acid emulsions or with a blend of chitosan and O, O′-dipalmitoylchitosan (DPCT)	5 mL aliquot chitosan-based coating solution was applied on format sheets with dry deposit of ~1.6 g·m^{-2}.	Chitosan – palmitic; 239 and 170 g·m^{-2}d^{-1} versus 241 and 161 g·m^{-2}d^{-1} DPCT; 441 and 442 g·m^{-2}·d^{-1} KIT 6-8/12	110°–120°	Blends of chitosan with palmitic acid and DPCT enhance its barrier and antimicrobial properties.	(Bordenave et al., 2010)
Chitosan reinforced with different concentrations of MCC: coating on kraft paper	Chitosan-MCC solution was applied as multilayer coating on paper sheets using RK Control K303 laboratory coater (2 m/min).	Decreased from 99.6 g/m^2 to 35 g/m^2	Reduced porosity of the kraft paper almost twice compared to uncoated samples	WVTR, porosity, and water absorption were reduced significantly in coated samples. Besides, the gloss value increased in coated samples.	(Akter et al., 2020)
Caseinate and caseinate	Chitosan (7, 10, and 12 % w/w) were applied as bilayer coatings over paper using automated coater (KCC 101, RK Print-Coat).	Decreased from 18 to 2 g mm m^2 d^1	Not described	Water vapor permeation was reduced significantly by the addition of caseinate/chitosan. Besides the coating also helped with the mechanical properties of the substrate.	(Khwaldia et al., 2014)
Chitosan	Six coat weights of chitosan solution within the range from 1.2 to 5.2 g/m2 were applied on paper using K101 Control Coater.	Grease resistance was calculated according to TAPPI T-454 as a function of air permeation. Max 1800 s.	Oxygen permeation was reduced from 660 nm/Pa s to <0.001.	Different coat weights displayed different effects on the barrier properties of paper. Gas and air permeability was recorded lowest at 5 g/m^2.	(Kjellgren et al., 2006)
Chitosan-acetic acid salt/whey protein isolate/whey protein concentrate and gluten wheat protein	Chitosan based coating solutions were applied on paperboard using Curtain coating approach (band speed, 10 cm/s).	Not described	Reduced from 1.09 day/m^2/atm. to 0.153 day/m^2/atm. Besides, air permeability was also reduced.	Chitosan-acetic acid salt/whey protein isolate/whey protein concentrate, and gluten wheat protein solutions were applied on the paper board using compression coating and curtain coating methods. Chitosan displayed good barrier and mechanical results in all coating conditions.	(Gällstedt et al., 2005)
Chitosan and gelatin	Chitosan-gelatin solutions (0.5, 1.0, 1.5, 2.0 and 2.5 %) were applied on paperboard samples by immersing in coating solutions for 30 s followed by drying at 105 °C.	Not described	Air permeability reduced from 375 ± 15 to 65 ± 6.	Coating bagasse paper with chitosan and gelatin displayed positive effects on the final barrier and mechanical properties of the substrate.	(Nassar et al., 2014)
Chitosan palmitic acid emulsion	4 wt% chitosan-palmitic acid emulsions (0.25, 1.00 and 2.00 wt%) emulsions were applied on kraft paper using 40 μm wire bar coater.	Significantly lower the WVTR (by ca 43–51 %) and water absorption capacity (by ca 35–41 %).	Air permeability was reduced by 8-fold.	Chitosan emulsion coating significantly enhanced the barrier (air permeability, WVPR, and water adsorption) and mechanical properties.	(Reis et al., 2011)
Beeswax-chitosan emulsion	Chitosan solutions containing beeswax (30 wt %, 60 wt% and 90 wt%) were applied on paper using K303 Multicoater (10 m/min).	WVTR reduced from 2797.2 g/m^2/d to 495.6 g/m^2/d.	From 118.0° ± 0.6 to 138.3° ± 0.4	The incorporation of beeswax in chitosan at different concentrations (10 to 90 wt%) and different drying conditions significantly reduced the barrier property of the coated paper.	(Zhang et al., 2014a)

Alkyl-chitosan/$CaCo_3$ derivatives	Alkyl chitosan and Alkyl chitosan-$CaCO_3$ composite solutions (30:70 w/w) were applied as surface coating on paper samples using Meyer-Rod method.	WVTR of paperboard was significantly reduced in the case of chitosan derivative containing shortest alkyl chain and highest substitution degree.	From 73.5° ± 2.6 to 132.6° ± 1.9	Alkyl-chitosan/$CaCo_3$ derivatives significantly reduced the water adsorption and WVTR of paperboard.	(Nicu et al., 2013)
Chitosan/Montmorillonite (MMT)	2 wt% chitosan solutions containing MMT (1 %, 1.5 %, 2 %, 2.5 %, and 3 % (w/v)) were surface coated on kraft paper using rod coating approach (rod no. 8).	The KIT rating was recorded on 9/12 for paper coated with chitosan-MMT	WCA decreased by 10.4–16.2° compared to control (decreased by 24.6°). The OCA decreased by 6.4–6.8°, compared to the control (decreased by 11.6°).	Chitosan-MMT composite coating significantly enhances grease resistance. Also, the air permeability and water and oil contact angles were significantly enhanced.	(Wang et al., 2021)
Chitosan	Chitosan with different degrees of acetylation (2 % and 48 %) was surface coated on cardboard using a 60 μm bar (TKB Ericken, Brazil).	Excellent oil barrier was observed in coated samples (KIT >8). WVTR value decreased from 298.17 ± 3.34 to 280.69 ± 2.92 (g H_2O/m^2day).	Not described	Chitosan with 2 % DA presented better water barrier and mechanical properties. Distributions of acetoglucosamine and glucosamine affect more hydrophilicity than quantity.	(Gatto et al., 2019)
Carboxymethyl cellulose (CMC)/chitosan (Ch)	1 % w/v. chitosan solution containing 1 %, 2 % and 3 % CMC was applied on paper using three different coating approaches namely mono-and bi-layers methods. K-coater was used to deposit the layers.	WVTR was reduced to 2 g $m \cdot m^{-2} \cdot d^{-1} \cdot kPa^{-1}$	Not described	Bilayer coating of carboxymethyl cellulose (CMC)/chitosan (Ch) bilayer enhanced the barrier behaviour from 1 % to 3 %, where the reduction percentages were from 25 to 37 %, respectively.	(Basta et al., 2015)
Chitosan/zein/essential oil	1 % w/v. chitosan solution and 30 % w/v. solution were applied on paper as dual layer surface coating using wire-wound bars.	Excellent water (Cobb60 value of 2.18 g/m^2) and oil barrier properties	Not described	Paper was coated with a solution of chitosan, zein, and rosemary in different combinations. Coating resulted in increased oil barriers and reduced water permeability. Besides the coated samples revealed high thermal stability.	(Vrabič Brodnjak and Tihole, 2020)
Water-soluble chitosan derivative	Chitosan solutions (1 % acetic acid and water, respectively) at 2 % (w/v) were applied on paper using size press machine (20 m/min).	Water vapor permeability decreased 45 % (3.24 ± 0.04 to 1.85 ± 0.06 10^{-2} mm g/(h·kPa·m)) after 5 coats of chitosan.	Chitosan and water-soluble chitosan promoted a considerable and progressive decrease in the air permeability	*Eucalyptus globulus*-based paper sheets were coated with chitosan and water-soluble chitosan derivatives. Depending on the number of coats bother CH and WSCH displayed a positive impact on decreasing the WVP and air permeability.	(Fernandes et al., 2010)
Chitosan-Zein	Chitosan solution composited with different concentrations of zein was applied on kraft paper substrates as layer-by-layer coatings using K303 Multi Coater.	KIT ratting was observed as 12/12 for coated (two coating layers) paper samples compared to the uncoated paper which had a value of 0/12.	The water contact angle increased from 53.5 ± 1.3° to 96.1 ± 5.8°. Cobb 60 value of 4.88 g/m^2.	Kraft paper was coated with chitosan and zein. Barrier properties were significantly improved when the paper was coated with bother polymers. Besides, the mechanical strength of coated paper is retained after coating.	(Kansal et al., 2020b)
Laccase-catalyzed chitosan-monophenol copolymer	Modified chitosan solutions (0.1 mg, 0.2 mg, 0.3 mg, 0.4 mg, 0.5 mg, and 0.6 mg) in 100 mL acetic acid solution (2 %, v/v) were applied on paper sheets using a brush via a surface sizing approach.	The sizing degree of base paper increased from 0.2 s to 331.7 s at the coating weight of 1.53 g/m^2. Cobb values decreased from 110.06 g/m^2 to 48.66 g/m^2	Not described	Enzymatically modified chitosan (hydrophobic monophenol compound (4-hexyloxyphenol, HP)) was used as a coating agent. Significant enhancement was recorded in hydrophobic properties due to the interaction of the hydrogen bonding between the copolymer coating and the cellulose fibers.	(Ni et al., 2021)
Chitosan/proteins/beeswax	Chitosan solutions with beeswax, and proteins were applied on the surface of paper as a bilayer coating using K303 Multicoater (10 m/min).	WVTR decreased from 171.6 to 52.8 g/m^2/d. The chitosan-bee wax-coated paper revealed good grease resistance (TAPPI standard T 507 cm-99).	Not described	Bi-layer coating of beeswax and chitosan was applied to the paper. Coating resulted in enhanced hydrophobic and grease resistance properties of paper.	(Zhang et al., 2014b)
Chitosan–graft–PDMS/zein coating for coating	Chitosan–graft–PDMS/zein solutions were applied on the surface of kraft paper using K303 Multi Coater.	WVTR decreased from ~1200 to ~400 g/m^2-day. KIT ratting increased from 0/12 to 11/12 after coating.	The water contact angle increased from 71.5 ± 0.5° to 121 ± 1.0° with a sliding angle of 46 ± 0.13°.	Kraft paper was coated with a solution of chitosan–graft–PDMS/zein. Coating significantly enhances the water and oil barrier properties of kraft paper.	(Hamdani et al., 2020)
Chitosan graft polydimethylsiloxane and poly (vinyl alcohol) coating	Chitosan-g-PDMS solutions (0:10, 80:20, 70:30, and 60:40) was applied on paper substrate using K303 Multi Coater (rod no. 8; wire diameter of 1.27 mm).	Cobb values decreased from 66.0 ± 1.8 g/m^2 to 24.6 ± 1.3 g/m^2. The KIT rating was improved from 0/12 to 7.6/12.	The water contact angle was increased from 84 ± 0.8° to 119 ± 6.3°. The oil contact angle increased from 27 ± 2.8° to 77 ± 2.6°.	This study reports that up to 80–90 % of PVOH blended with 10–20 % chitosan-g-PDMS imparts excellent water and grease-resistant paper coating, thus offering a significant improvement over the previously published work.	(Nair et al., 2021)

properties, thanks to their inherent scattering and reflective, low absorbency, and high dispersive nature (Sanchez-Garcia et al., 2010). Natural clay particles have been incorporated into chitosan-based films to enhance their UV barrier properties. Lei et al. (2021) reported a 36.3 % increase in UV (at 300 nm) barrier properties of chitosan when incorporated with clay. Similarly, lignin nanoparticles have emerged recently as favorable UV barrier material as it contains various UV absorbing functional groups such as phenolic unit, ketone, and chromophores. Owing to the presence of these functional groups, lignin displays excellent UV and antioxidant properties when applied to a packaging matrix. (Rukmanikrishnan et al., 2020) incorporated 10 wt% lignin into gellan gum/hydroxyethyl cellulose composite. UV barrier results revealed 100 % protection against UVB (280–320 nm) and 90 % against (320–400 nm). In another study, Ahmed et al. (2017) introduced graphene oxide nanosheets to chitosan films at different concentrations. Results revealed a significant decrease in UV transmittance through chitosan films containing zinc oxide nanosheets.

4. State of art of biopolymers-based barrier technologies

4.1. Chitosan

Chitosan is among the most favored biopolymers successfully drawing the attention of industries and researchers, thanks to its inherent properties such as biodegradability, biocompatibility, antimicrobial and antioxidant, non-toxicity, and excelling film-forming ability (Oladzadabbasabadi et al., 2022). Chitosan can be easily obtained after a simple process of deacetylation (to varying degrees) of chitin. It is an economic polymer due to the large availability of cheap raw materials. Chitin can be isolated from arthropods, crustaceans, Mollusca, and microorganisms. Currently, the waste of seafood such as the exoskeleton of crabs, lobster, and shrimps is among the main sources of chitin isolation (Garavand et al., 2022). According to the Web of Science, 1775 reports (research articles; 1634, Review articles; 90, Proceeding papers; 70, Early access; 27) can be found about chitosan-based films and coatings in the year 2017–2021 (5 years). These numbers are rapidly increasing as in our earlier review article the total number of records published on the same topic was 1860 in the year between 2007 and 2017 (10 years) (Mujtaba et al., 2019). This two-time increase in the number of published records outlining the importance of chitosan for different applications (mainly in the food industry).

Historically, the discovery of chitin traces back to a French Professor of natural history Henri Braconnot in 1811, when he noticed an insoluble part of a mushroom in an alkaline solution. Professor Henri Braconnot named this insoluble fraction “fungine”. Later, in 1823, Antoine Odier isolated alkaline insoluble fraction from the insect cuticle and named it “chitine”. The word “chitine” originally originated from the Greek word “Khiton” meaning envelope. The presence of nitrogen in chitin was reported by Jean Louis Lassaigne (Crini, 2019a). Finally, in 1859, Prof. C. Roguet extracted the deacetylated form of chitin by treating chitin with a concentrated solution of potassium hydroxide. Prof. C. Roguet named the isolate “modified chitin”. The term chitosan was first used by Hoppe-Seyler in 1894 when he treated to crab, spider, and scorpion shells with potassium hydroxide solution (180 °C) followed by dissolution of the isolate in dilute acid solution (Crini, 2019b). Chemically chitosan formed two sub-units as D-glucosamine and *N*-acetyl-D-glucosamine connected linearly with each other via 1,4-glycosidic bonds (Khajavian et al., 2022). The physical properties of chitosan such as solubility, viscosity and biodegradability are defined by its deacetylation degree. It is a cationic polymer, offering antimicrobial resistance against a large set of pathogenic and food-borne microorganisms (gram-positive and gram-negative bacteria and fungi). Owing to such attributes, chitosan is employed is many biomedical applications such drug delivery and wound healing (Günyaktı et al., 2022; Karakeçili et al., 2022). Besides, due to its crystallinity and the presence of hydrogen bonds among molecular chains, it supplies an excellent barrier against oxygen permeation. The positive charges on amino acid groups enable chitosan to serve as a grease resistance coating material for different surfaces (Sharif et al., 2018).

So far chitosan has been extensively investigated alone or in combination with plant extracts, essential oils, and other polymers (composites) such as alginate (Yuan et al., 2007), cellulose (HPS et al., 2016), chitin (Salaberria et al., 2015), PCL (Swapna Joseph et al., 2011), PLA (Claro et al., 2016) and starch (Lozano-Navarro et al., 2018), etc., to enhance its mechanical, barrier, antimicrobial and antioxidant properties. The cationic nature of chitosan and the presence of a substantial number of polar groups such as NH_2, NH, OH, C═O, and C—O—C— —, over the polymeric backbone, make it compatible with the above-discussed polymers (Mujtaba et al., 2019).

Chitosan has been extensively tested as a potential candidate for green and sustainable food packaging. Besides, many advantages, chitosan also exhibits numerous inherent drawbacks such as low hydrophobicity, and low mechanical and thermal strength (Wang et al., 2018a). These drawbacks arise as a major constraint to utilizing chitosan on an industrial scale as a barrier enhancer in food packaging. For this purpose, chitosan was combined with other biopolymers (cellulose/nanocellulose/carboxymethyl cellulose, curdlan, starch, genipin, chitin), plant/animal proteins (zein, whey-protein, gelatin, caseinate) waxes (beeswax, essential oils) and minerals (montmorillonite and diatomite), etc. (Mujtaba et al., 2019; Yu et al., 2021). Different strategies such as cross-linking, graft copolymerization, composite/blending, and enzymatic treatments were employed to enhance the physicochemical and biological attributes of chitosan (van den Broek et al., 2015). As it is known from the above-mentioned statistical figures, many studies have been carried out on chitosan-based films checking their barrier properties. However herein we mainly target the coating potential of chitosan-based composites for paper board packages. For reference, we also include some film studies in the table.

A synopsis of the effects of chitosan as a coating material alone or in combination with other polymers, proteins, and lipids on different barrier properties has been provided in Table 2.

4.2. Cellulose based composites

Cellulose being a structural polymer of plants and bacteria is the most abundantly found renewable and biodegradable biopolymer in nature (Mujtaba et al., 2017b). Currently, the major sources for commercial production of cellulose include; plant/wood pulp (currently 90–95 % of cellulose pulp is produced from wood) (Laftah and Wan Abdul Rahman, 2016), lignocellulosic biomass from agricultural waste (attention has diverted to this source due to its low starting value and easy generation) (Boufi, 2017; Mujtaba et al., 2017a; Mujtaba et al., 2018), cotton, flax (Mujtaba et al., 2017b), jute, and kenaf (Pennells et al., 2020). Cellulose is a linear polysaccharide that consists of the repeating units of cellobiose linked through a β-1,4 glycosidic bond. Cellulose has been widely utilized in different applications such as biomedicine, cosmetics, agriculture, paints, drilling muds, composite materials, absorbents in hygiene products, and food packaging (most commonly as a coating layer for cardboards) (Fig. 4) (Habibi et al., 2010). This widespread interest can be attributed to numerous advantages offered by cellulose, such as easy availability from renewable resources (wood, cotton, lignocellulosic biomass etc.), barrier properties, high surface area, desirable mechanical strength, tunable chemical structure, biocompatibility, and biodegradability (Rodionova et al., 2011; Tajeddin, 2014).

Cellulose is applied in different forms, i.e., cellulose nanofibrils (CNF), cellulose microfibrils (CMF), nanocrystalline cellulose (NCC), cellulose nanowhiskers (CNW), and microcrystalline cellulose (MCC). MCC is composed of crystalline and amorphous regions that are randomly dispersed along the fiber lengths. In crystalline regions of MCC, the polymer chains are firmly compact, while the amorphous regions are more prone to chemical and enzymatic interactions. MCC and NFC are produced via mechanical grinding or homogenization. NCC is a nanoscale crystalline form of cellulose, which is extracted by the enzymatic or acid hydrolysis of biomass. NCC possesses a rod-shaped structure with a diameter in the range of 1–100 nm and a length in the range of 10–100 nm.

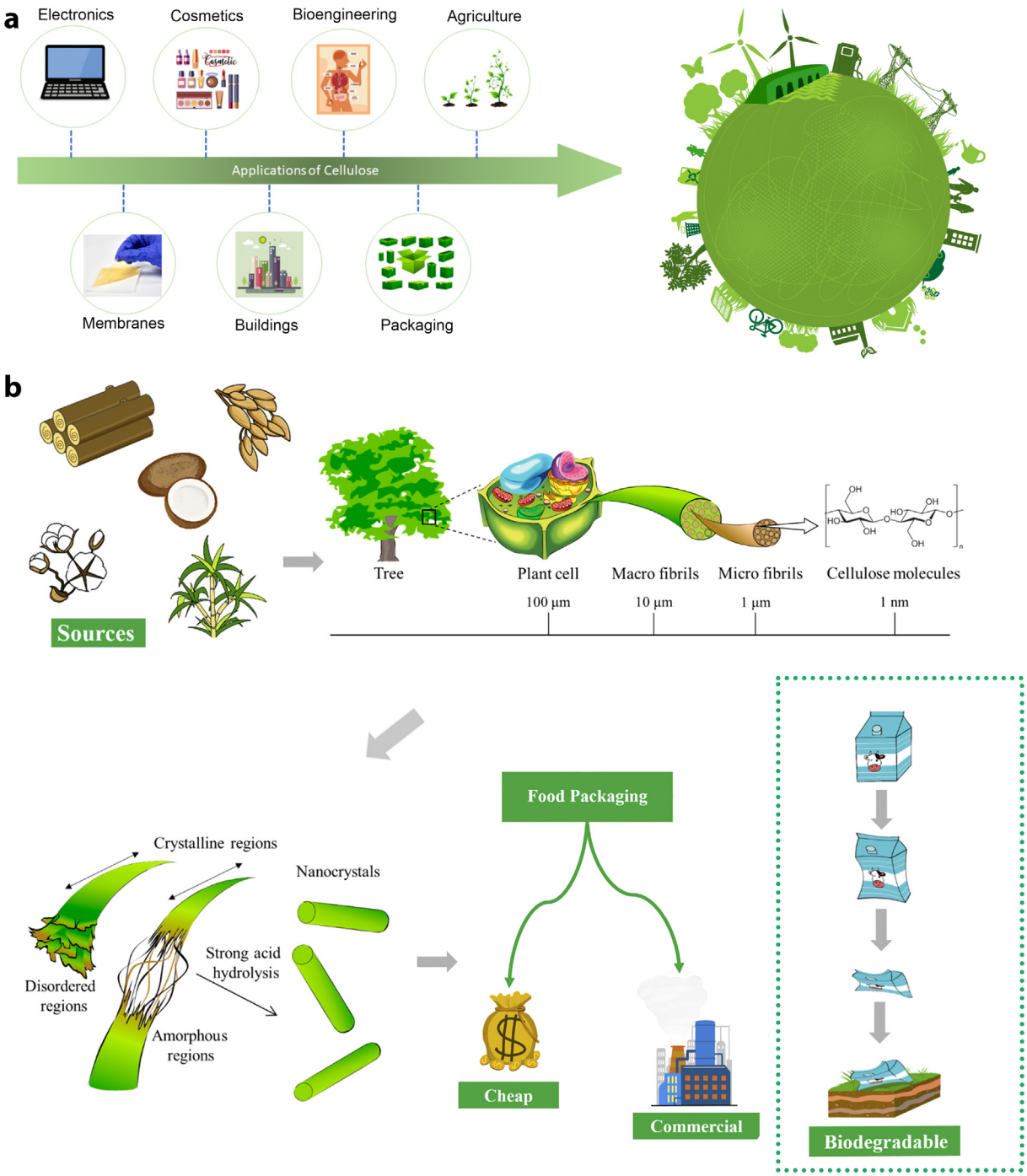

Fig. 4. Major sources and applications of cellulose; a) Applications of cellulose in different industries, b) sources of cellulose and its applications in the food packaging industry. (Reprinted from Liu et al. (2021) and Miyashiro et al. (2020) with permission of MDPI and Elsevier.)

Due to the renewable source and favorable chemical/physical properties, cellulose is among the strongest candidates to replace the other petroleum-based synthetic polymers that are currently used by the food, biomedicine, cosmetic, and paint industries (Table 3). When applied as a coating material on cardboard/paper-based packaging, cellulose can significantly enhance barrier properties by reducing the migration of permeants across the packaging surface. As given in Table 3, cellulose has been applied alone and with other polymers for the enhancement of barrier properties. Application of nano and microfibrillated cellulose at a concentration ranging between 1 and 3 % can significantly enhance the WVP and WRV of paper/cardboard surfaces. Besides, multilayer coating of cellulose nanofibers and esterified CNFs can significantly contribute to the enhancement of oxygen transmission rate and water contact angle.

4.3. Lignin

Currently, enormous research has been focused on the efficient conversion of biomass components to biofuel and other value-added products (Mahmood et al., 2019). The valorization of lignocellulosic biomasses can be a solution to many future problems (Korányi et al., 2020). Lignins are currently the most favored renewable polymers, that can be utilized in several application areas such as biomedicine, cosmetics, energy, food, coatings,

Table 3
Cellulose-based coatings for enhancement of the barrier properties of cardboard/paper-based packaging.

Cellulose/derivative	Concentrations/Application methodology	Effects on barrier properties	Important outcomes	References
Nanofibrillated cellulose (NFC)/chitosan nanoparticles (CHNP) nanocomposites	Manual coating OF NFC/CHNP mixture containing 10 % CHNP.	WVP increased by 15 %, Water absorption reduced by 33 % (Cobb test), and Excellent greaseproof properties (oil penetration time increased from 6 s to 78 s)	Coated paper sheets revealed an increase in tensile strength, tensile modulus, and strain at break of 14 %, 21 %, and 30 %, respectively. Besides, a decrease in porosity was recorded as 17 % and 19 % in the case of NFC and NFC/CHNP, respectively.	(Hassan et al., 2016)
Nanofibrillated cellulose (NFC)	0.10, 0.20, 0.30, 0.40 % of NFC along with binders and pigments. The coating was performed through a rod coating setup.	Water retention value decreased noticeably with increasing NFC concentrations. WRV of 250.0 g/m^2, to 158.71 g/m2 at an addition of 0.40 % NFC. The water absorption values were decreased from 27.50 g/m^2 to 25.0 g/m2 and 24.0 g/m2, at 0.30 % and 0.40 % NFC respectively. This decrease in cobb values can be ascribed to the fact that the addition of NFC reduced the gap size of coated paper.	Coating of NFC led to a reduction in Cobb value, improved the air resistance, and enhanced the tensile of coated paper. 0.30 %–0.40 % was determined as the optimum concentration for coating.	(Jin et al., 2021)
Cellulose nanofiber (refiner produced material (rCNF) and cellulose isolates from the ultra-fine grinder (gCNF) and)/carboxymethyl cellulose blends	1–3 wt% CNF suspensions with and without carboxymethyl cellulose (used as an additive in this experiment) were applied on paper using a rod coater (50 mm/s).	Gravimetric water retention values decreased with an increase in solid content from 1.5 to 3 %. However, the addition of CMC increases the GWR values due to the water solubility of CMC. gCNF showed higher viscosity than rCNF. Increasing coat weight from 1.6 to 2.6 g/m^2 enhanced the air resistance (80 to 1400 Gurley *sec*) and for coat weights 6.9 and 7.8 g/m^2 the air resistance was recorded as 740 and 4700 Gurley sec for rCNF and gCNF, respectively. No noticeable reduction in WVTR was recorded for coated paper.	CNF application significantly improved the barrier properties of coated paper. Results revealed that 2 % CNF suspension was not spread out evenly on the substrate surface, however using CMC, 3 % CNF was successfully applied on the substrate surface (evident from SEM).	(Mousavi et al., 2017)
Microfibrillated cellulose (MFC) coating on cardboard	2 % MFC suspension was applied on cardboards using bar coating (5 cm^{-1}). The process was repeated 5 times to deposit 5 layers.	Air permeability was not affected by coating and remained almost unchanged (0.17 ± 0.01 to 0.18 ± 0.01 cm^3/m^2·day). Water adsorption increased from 43 ± 7 to 114 ± 7 g/m^2. KIT values increased from 0 to 2.5 ± 0.5.	Coating of MFC on cardboard samples enhances the bending stiffness and compressive stiffness by 30 %. However, MFC did not contribute to the enhancement of barrier properties.	(Lavoine et al., 2014)
Acetylated cellulose supplemented with cinnamaldehyde (CIN); kraft paper coating	Solution of acetylated cellulose/CIN was prepared at different concentrations i.e., 2 %, 4 %, 6 % and 8 % v/v. Coating Weight and thickness were kept at 20.2 ± 0.9 g/m2 and 107.7 ± 1.7 μm. The coating was performed by hand lay-up technique.	KIT values increase from 1.0 to 12.0. Water absorption decreased from 41.8 ± 3.5 to 1.5 ± 0.2 (10^{-12} g m/m^2·s·Pa). oxygen transmission rate decreased from 2.9 ± 0.2 × 10^{10} to 2.6 ± 0.2 × 10^3 (cm^3/m^2·d·0.1 MPa).	Coating acetylated cellulose with CIN oil enhanced the mechanical properties of kraft paper. Besides, notable enhancement was recorded in barrier properties, especially for the water barrier rate up to 96.4 %.	(Zhang et al., 2021a)
Cellulose stearoyl ester (CSE) coating for paper sheets	Coating weight 0.5–23.6 g m^{-2}. Coating solutions with concentrations of 0.58, 1.15, 2.31, 4.18, 5.54, and 6.52 wt% were applied onto paper sheets (14.1 × 14.6 cm^2) using an automatic film applicator (ZAA 2300, Zehntner Testing Instruments, Switzerland).	Contact angle values increase from ≈15 to 109 ± 2°. WVTR values declined from 514.80 to 27.74 g m^{-2} d^{-1}. The barrier ratio of coated paper to uncoated paper was recorded as >90 %.	5.2 g m^{-2} of coating completely covered the paper surface with overall roughness of 2.327 nm. Coating resulted in decreased tensile strength and increased elongation at break. The water vapor barrier properties were enhanced after coating.	(Wang et al., 2020)
Multilayered coatings of hybrid gibbsite nanoplatelet/cellulose nanocrystal for kraft paper	Multilayer hybrid coating was applied on four different substrates including uncoated kraft cardboard of 225 g/m^2. Coating solutions were applied by dipping the substrates.	The oxygen transmission rate was decreased by 75 %.	Air permeability was reduced by coating multiple layers of gibbsite nanoplatelet/cellulose nanocrystal.	(Chemin et al., 2019)
Cellulose nanofibril (CNF)/clay composite	1.4 % CNF suspension with 3 and 5 % clay was spray-coated (5 bar and 15 cm distance) on paper sheets. Corona treatment was also applied to the samples before coating.	WVTR reduced from 28.55 ± 0.7 to 4 ± 0.2 (g m^{-2} day). OTR values were not improved because of the incomplete closure of the base paper.	Corona discharge enhanced the water repellency of base sheets. Increasing the spray time to 30 to 50s enhances the barrier properties of coated kraft paper samples.	(Mirmehdi et al., 2018)
CNF coating on paper	Paper samples were coated with 1.5 wt% or 3 wt% CNF as a single or double layer.	Coating with 1.5 wt% resulted in more uniform coat layers compared to 3 wt%. The air resistance of paper coated with 2 coats of 1.5 % of CNF was greater than samples coated with a single coat of 3 wt% CNF. The water absorption rate and roughness in paper coated with a double layer of 1.5 wt% CNF was less than that of paper coated with a single layer of 3 wt% CNF.	NFC coating with 1.5 wt% demonstrated more uniform coating layers and enhanced barrier properties compared to 3 wt% NFC coat layers.	(Afra et al., 2016)
Carboxymethyl cellulose/cellulose nanocrystals with silver nanoparticles as a coating for paper	Paper was coated with 2 g of CMC, CNC@AgNPs (0, 1, 3, 5, and 7 wt% based on CMC).	The tensile strength of coated paper increased 1.26 times. WVP and air permeability of coated paper demonstrated 45.4 % and 93.3 % reduction respectively. The antimicrobial properties of coated paper are enhanced after coating.	Coated paper samples demonstrated enhanced barrier properties. These samples were also tested for strawberry storage and the results were quite promising.	(He et al., 2021)

composites, etc. (Fig. 5). The main reason behind this increasing interest is the imminent availability as a bioproduct of advanced biorefineries (Chio et al., 2019). The biosynthesis of lignins occurred from the oxidative coupling of *p*-hydroxycinnamyl alcohol monomers (*p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) type phenylpropane (or C_9) units) and other related compounds (Boerjan et al., 2003). The chemical makeup of lignins displays variation depending on the wood source. Softwood lignins are largely comprised of G-type with trivial amounts of H-units. Hardwood lignins contain different ratios of S- and G-units (S/G ratio) (Calvo-Flores and Dobado, 2010). Non-wood lignins are mainly HGS-type lignins. In all these lignin types, the monomers are attached through the various ether and C—C bonds. Lignins exist in two main types, i.e., native and technical. Native lignins are isolated from Milled Wood Lignin and cellulolytic enzyme lignins (Guo et al., 2017). The monomers of native lignins are attached through β-O-4 linkages, followed by 5-5, β-5 (SW), β-β (HW), etc. Native lignin has a highly branched and crossed-linked structure (~36 % of lignin units share these linkages) (Chio et al., 2019). The highly branched structure of native lignin remains intact and even enhanced during the conversion of native lignin to technical lignin. Technical lignin is obtained after the chemical treatment of biomass. Currently, technical lignin has been utilized in most industrial and other commercially relevant applications (Ekielski and Mishra, 2020). Technical lignin contains a dwindling number of native lignin functional groups, however, the catalyzed biomass hydrolysis results in the formation of new functional groups on the structure (Chakar and Ragauskas, 2004). Technical lignin is more chemically heterogenous, thanks to the presence of different structural moieties. Technical lignins are further classified to several types depending on the pulping sources (e.g., kraft lignin, soda lignin, organosolv, etc.) (Vanholme et al., 2008). Technical lignins can be further structurally upgraded using different chemical modification tools such as alkylation and acetylation. These upgrades are carried out to efficiently use technical lignin in different applications such as composite formations, surfactants, sorbents, etc. (Vanholme et al., 2008). Currently, lignosulfonates are dominating the market with around 80 % utilization in commercial applications and processes. However, with growing interest in the lignin market, the production of kraft lignin is also making notable growth progress in terms of market capturing. This growth can be ascribed to lower production costs and higher reactivity of kraft lignin (Dessbesell et al., 2020).

Lignin is one of the most abundant polymers next to cellulose. A substantial proportion of lignin has been produced as black liquor in the paper and pulp industry. Around 95 % of this lignin is directly used at the same factories as burning fuel. The remaining 5 % is utilized in different industrial applications (Lievonen et al., 2016). On average around 50 to 70 million tons of lignin are produced every year (Saratale et al., 2019).

The emerging application areas of lignin include fuels (Cheng and Brewer, 2017), adhesives (Gong et al., 2022), paper coating (Zhang et al., 2021b), controlled release agents (agrochemicals) (Dos Santos et al., 2021), health (drug encapsulation and delivery, obesity, diabetes, cancer) (Ullah et al., 2022), cosmetics (Tran et al., 2021), coating for furniture etc. (Henn et al., 2021). Despite all these interesting applications, the larger particle size, heterogeneity, low rate of dispersibility and asymmetrical morphology are the major limiting factors in the efficient utilization of lignin as a high-value material (Yadav et al., 2022). For this purpose, lignin is transformed into nanoparticles by following various chemical routes. Nanosized lignin materials offer several advantages, i.e., degradability, uniform size, dispersibility, high surface area, etc. (Schneider et al., 2021). Lignin nanoparticles (LNPs) can be produced using different chemical strategies such as antisolvent precipitation, solvent exchange, ultrasonication, interfacial cross-linking, polymerization, and biological pathways (enzymes) (Zhang et al., 2021d).

Lignin-based materials have been applied as barrier enhancers on cardboard and paper packaging systems. In a study by (Hult et al., 2013), Tall oil fatty acid (TOFA) functionalized lignin has been applied as a barrier material on cardboards. Lignin was esterified to enhance its film-forming ability by activating the thermoplastic character. Coated paper samples revealed a notable decline in WVTR (from 840 g/m^2 to 260 $g/m^2 \times 24$ h) and oxygen transmission rate (OTR). In another study by (Antonsson et al., 2008), a hydrophobic paper coating was prepared by using low molecular weight lignin and linseed oil. The coated paper samples revealed enhanced hydrophobic properties. Lignin-containing cellulose nanofibers are also an economical and efficient barrier material alternative to plastic-based polymers. Tayeb et al. (2020), utilized lignin-containing cellulose fibers as a barrier coating material on paper substrates. LCNF-based coating resulted in excellent oil barrier properties with KIT = 12. In several studies, researchers have taken good advantage of a composite forming property of lignin and tested different lignin-based blends and composites as a barrier coating material for paper substrate. Lignin/tannin/ZnONP (40 % lignin, 15 % tannin, and 10 % ZnONPs) composite coating was prepared and applied to the packaging material. Coating resulted in high mechanical strength, moisture resistance, lower air permeability, and heat endurance (Xie et al., 2021). In another work, lignin-containing fractions (15 % best performing concentration) of lignin-vinyl acetate copolymers were applied on paper as barrier coating material. According to the results, the hydrophobicity, air permeability, and mechanical attributes of coated paper samples were improved significantly (Zhang et al., 2021b).

Considering the literature reports about the application of lignin as a barrier coating material, a huge unexplored potential is still present in this area. Lignin nanoparticles can be efficiently used as a barrier coating material for cardboard and paper substrates.

4.4. Modified starches

Starch is an inexpensive and eco-friendly natural polymer. It is a versatile polymer offering easy depolymerization with high control (Copeland et al., 2009). Starch can be extracted from a variety of plant sources such as cereals (barley, sorghum, wheat, corn, rye, and millet), legumes (lentil, red kidney bean, mung, pinto bean, etc.), root and tubers (potato, cassava, yam, cocoyam, and sweet potato) and immature fruits (banana, plantain, mango, and pawpaw) (Laurentin et al., 2003; Moorthy, 2004). Starch exists in granule form in the stem, leaves, and fruits. Depending on the source, starch granules vary in shape and size. Chemically, starch is made up of two main components, known as amylose (AM) and amylopectin (AP). AM and AP show different functionalities and properties, i.e., AM is known for the formation of tough gels and strong films (Parker and Ring, 2001). AP tends to disperse in water making stable gels and soft films. With an imperfect nature and a higher tendency towards retrogradation, native starch is not favored for industrial applications. The modification of starch makes it ready to use in industrial applications. Modified starches possess decreased retrogradation and gelling tendencies, improved paste clarity, texture, and excellent film-forming ability (Miyazaki et al., 2006). Different routes can be used for the modification of starches including physical, chemical, enzymatic, biotechnological, and the combination of these methods (Ghanbarzadeh et al., 2010).

Starch is among the key materials of the paper industry, thanks to its abundant availability and affordability. According to some estimates, globally paper industry is the largest utilizing industry of starch (Whistler et al., 2012). These starches are mainly used for surface treatment applications such as surface coating, sizing, and coating for enhancing the functional properties of paper (Li et al., 2019b). Starch is used as a coating co-binder in coating colors (a mixture of binders, pigments, and other additives) of paper along with synthetic latex-based binders such as poly (vinyl acetate), and polyacrylates, etc. (Bumanis et al., 2020). For this purpose, starch undergoes the necessary structural modifications to enhance its water solubility and decrease retrogradation. Native starch is modified through various modification strategies including, esterification, enzymatic degradation, cationization, oxidation, and acid degradation (Fonseca et al., 2021; Lemos et al., 2021). Among all these strategies, ultrasonic treatment is the most advantageous physical method, that causes splitting of α-1, 6-glycosidic linkages at the amylopectin branching points and achieves the least amylose degradation. Ultrasonic treatment of starch offers high selectivity and reduced use of harsh chemicals, serving as an eco-friendly strategy for the modification of native starch (Cao and Gao, 2020). Starch-

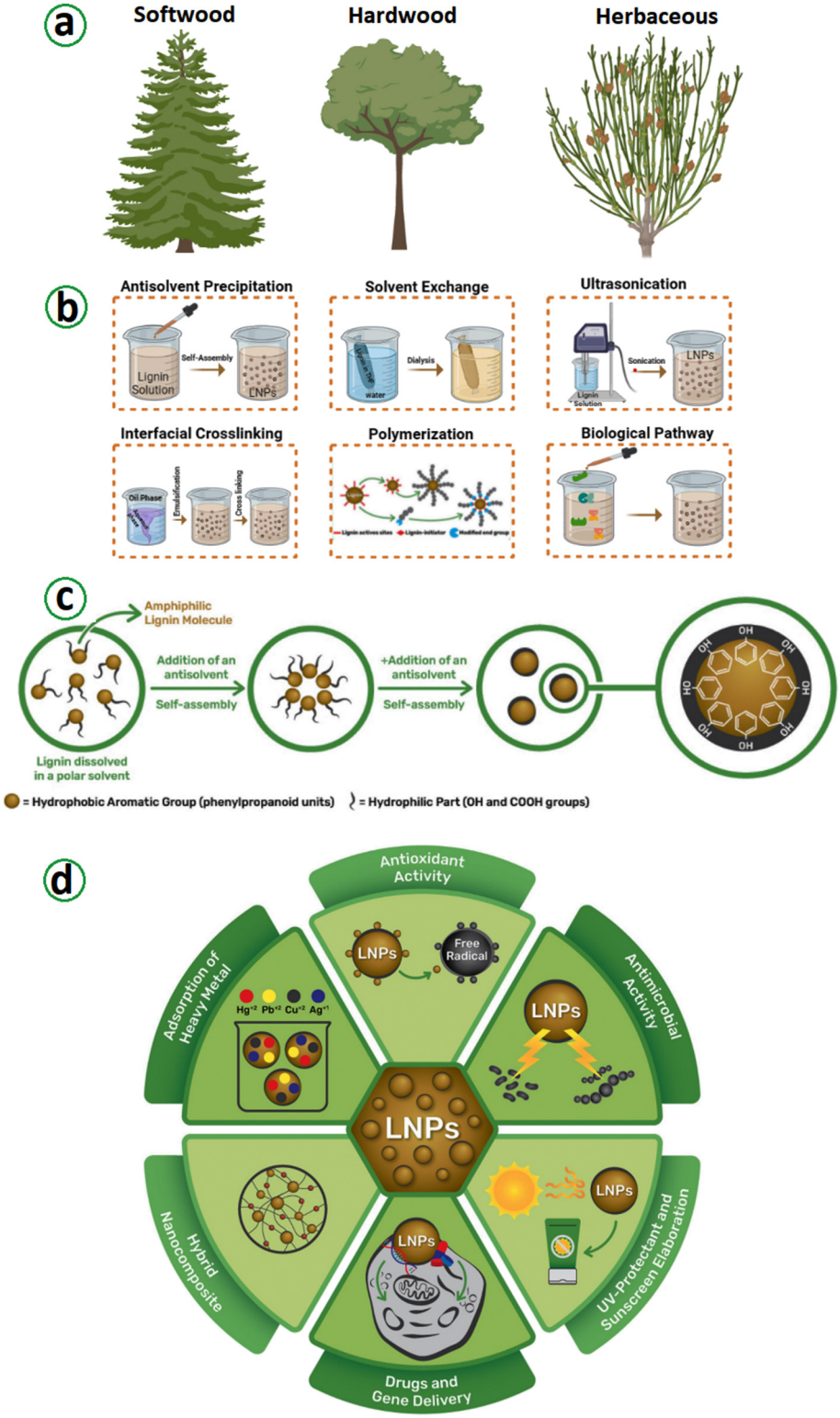

Fig. 5. a) Major sources of lignin, b) production methodologies of lignin nanoparticles, c) illustration of lignin nanoparticles formation mechanism, d) major application areas of lignin nanoparticles.
(Adapted and reprinted from (Schneider et al., 2021) with permission of Elsevier.)

based grafts are also used for the surface sizing of paper. Wang et al. (2011 prepared a graft copolymer of starch with styrene and butyl acrylate. The coating of copolymerized starch enhanced the thermal stability and water resistance of coated paper. In another study, starch-based salt inclusion complexes were prepared using high amylose cornstarch and hexadecyl- and octadecylammonium chloride. The complexes were applied to paper followed by NaOH treatment. The NaOH treatment transformed complexes to insoluble amine form, making the surface highly hydrophobic (contact angle 113°) (Hay et al., 2018). Starch nanocrystals and nanoparticles are also used as stabilizer and emulsifiers in different sizing agents such as

(alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) (Li et al., 2021).

Modified starch has been blended with other polymers and polysaccharides such as chitosan, cellulose, hemicellulose, and alginate for enhancing its barrier properties. Jung et al. (2018a, developed a functional antimicrobial coating by blending chitosan and starch with silver nanoparticles. Coating at 9:1 (by weight) resulted in enhanced mechanical, water, and oil resistance properties (Fig. 6). In a similar study, the poor mechanical and barrier properties of starch were enhanced by making a nanocrystalline cellulose-starch composite (0.1 to 0.5 %). Coated paper samples revealed improved air permeability resistance and optimal mechanical properties (Yang et al., 2014). A composite of starch and sodium alginate was prepared and tested on packaging paper. Results revealed that the grease barrier properties of coated papers were significantly enhanced compared to uncoated base paper (Jiang et al., 2014). Besides blending starch with other polysaccharides, it is reported that blending starch from different botanical origins can make a coating material for paper with enhanced barrier properties. Lee et al. (2017), synthesized starch composites for the reduction of air permeability of paper. Two types of modified starches i.e., hydrophilic α-waxy corn starch and hydrophobic aluminum octenyl succinate were composited together and coated on paper. Results revealed that mixing 20 wt% hydrophilic starch and 10 wt% hydrophobic starch significantly reduced the air permeability of paper. Thanks to the presence of OH groups in the structure of starch, it can be blended with several synthetic polymers. Similarly, Zhu et al. (2018, incorporated polyvinyl alcohol (a synthetic but biodegradable polymer) with starch to enhance the poor barrier properties of the starch coating film. As per expectation, PVA and starch made a successful composite enhancing the mechanical and barrier properties of coated paper.

4.5. Alginate

Alginate is a natural polysaccharide that is mainly isolated from brown algae (Phaeophyceae), including *Laminaria hyperborea*, *Laminaria japonica*, *Laminaria digitata*, *Ascophyllum nodosum*, and *Macrocystis pyrifera*). Alginate can also be isolated from some bacterial strains such as *Azotobacter*

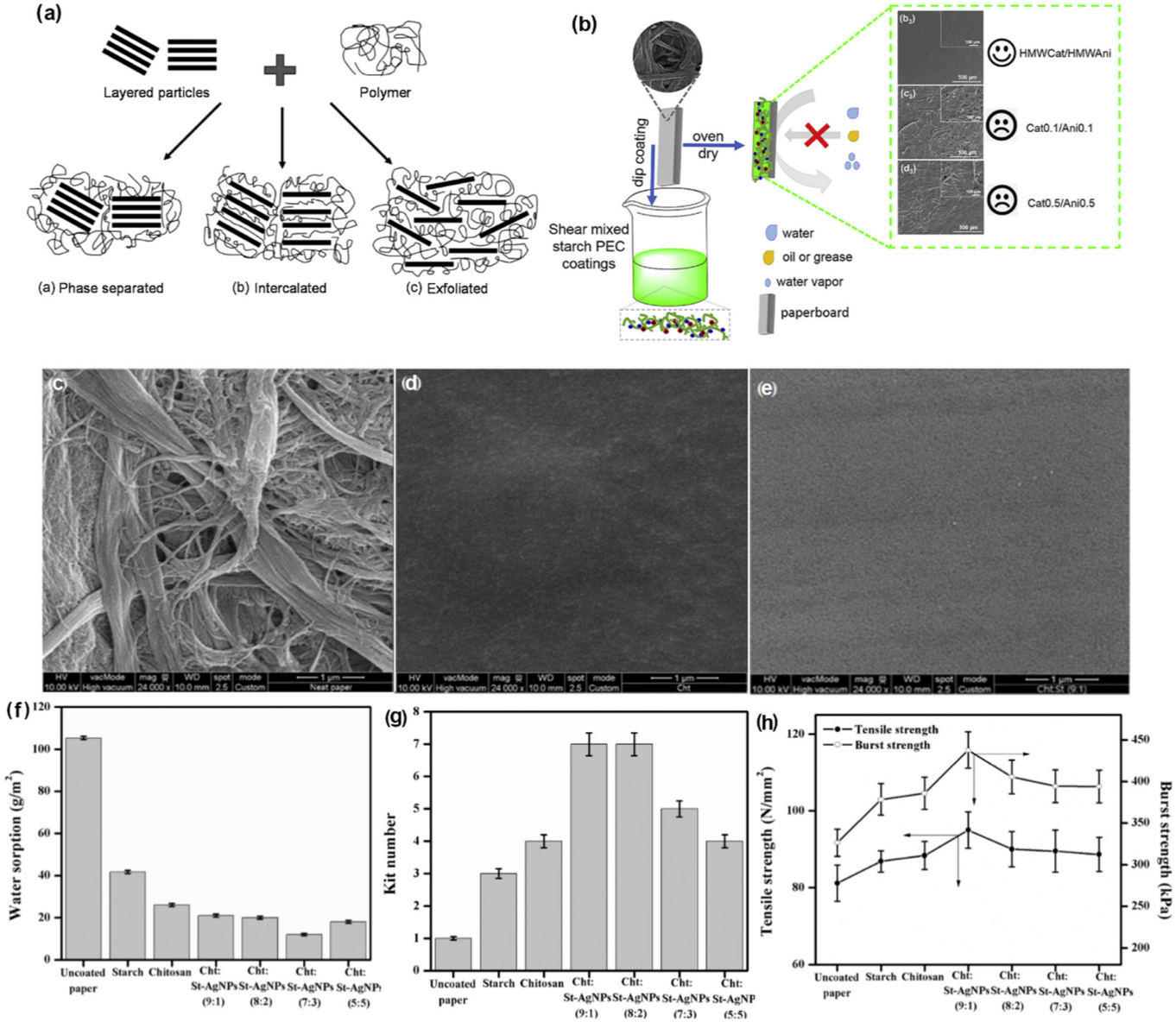

Fig. 6. Effects of starch coating on packaging materials; a) different forms of dispersions of layered particles in a matrix, b) starch-AgNP coating on paper enhanced the barrier properties of paperboard (adapted and reprinted from (Alexandre and Dubois, 2000; Jung et al., 2018b) with permission of Elsevier), c) uncoated paper, d) starch coated paper, e) starch-Ag coated paper, f) water adsorption properties of coated and uncoated paper, g) oil resistance of starch coated and uncoated samples, h) Tensile strength of starch coated and uncoated samples (adapted and reprinted from (Jung et al., 2018b) with permission of Elsevier).

vinelandii or mucoid strains of *Pseudomonas aeruginosa* (Lee and Mooney, 2012). Structurally, alginate is an unbranched, linear copolymer of β-d-mannuronic acid (M) and α-l-guluronic acid (G) residues linked by 1–4 glycosidic bonds. The structure of alginate can be divided into three sections, continuous MMMMMM, continuous GGGGGG, and alternating MGMGMG blocks. The ratio of M and G blocks varies according to the source. The different ratios of M and G blocks lead to different physicochemical properties (thickness and viscosity of polymer) of different alginates (Yang et al., 2011). Hydrogels of alginate can be formed by adding divalent cations (e.g., Ca^{2+}). Only G blocks are believed to be active in intermolecular crossing to form hydrogels. Na-alginate (E401), K-alginate (E402), NH_4^+-alginate (E403), and Ca^{2+}-alginate (E404) are different salts of alginic acid (Augst et al., 2006). The solubility of alginate is lower in low pH solutions. The molecular weight of commercially available alginate varies between 32,000 and 400,000 g/mol. High molecular weight alginate is good for gels with improved physical properties, however, the resultant solution is highly viscous (undesirable in industrial processing). Alginate is a biocompatible, non-toxic, and biodegradable polymer (Lee and Mooney, 2012). Alginate has a high scope of applications in biomedicine where it is used for drug delivery, protein delivery, wound healing, organ study, etc. (West et al., 2007).

In paper industry, alginate has been tested on a very limited level. The crosslinking ability of alginate with polyvalent metal cations (e.g., Ca^{2+}) is well exploited in many research reports. Rhim (2004), designed water-resistant alginate films by treating alginate films with $CaCl_2$ (treatment of alginate films by two methods i.e., immersion and mixing). The author reported a decreased water adsorption for films that were immersed in $CaCl_2$. The tensile strength was also enhanced by $CaCl_2$ treatment. In another report, Rhim et al. (2006) coated paper samples with alginate and soy protein. The effect of post-treatment with $CaCl_2$ on alginate and soy protein-coated paper barrier properties was investigated. Alginate is highly compatible with other polysaccharides, such as chitosan and cellulose. Chitosan is thought to be a good barrier material for paper; however, chitosan alone cannot enhance all the barrier properties of paper. To enhance the barrier properties of chitosan, alginate and cellulose ethers were mixed with a chitosan coating solution. Results revealed that chitosan formulations containing cellulose ether and alginate performed well and significantly enhanced the fat barrier of coated paper samples (Ham-Pichavant et al., 2005). Alginate has good antimicrobial and antioxidant properties. Owing to these properties, alginate has been used in designing functional paper packaging materials (Pan et al., 2021). In a similar study, antimicrobial paper packaging was prepared by coating paper with a blend of alginate, carboxymethyl cellulose, and carrageenan. Depending on coating materials and combinations, the wetting properties were improved. Samples coated with alginate and treated with $CaCl_2$ were observed to have good water resistance compared to other coating combinations (Rhim et al., 2006). Similarly, a composite blend comprised of collagen, sodium alginate, and polyvinyl butyral was fabricated. This tri polymeric composite was applied as a barrier coating on Ca^{+2} filter paper (Fig. 7). The composite coating displayed notable improvement in barrier properties i.e., water vapor resistance (48 $g/m^2 \cdot 24$ h), water resistance (31 g/m^2), and oil resistance (kit rating: 12/12) of coated filter paper (Jing et al., 2022).

4.6. Bio-polyesters (PHA, PBS, and PLA)

Polyesters like polyhydroxyalkanoates (PHAs), poly (lactic acids) (PLAs), and polybutylene succinates (PBSs) are considered as materials of the future. These renewable, biobased, and biodegradable polyesters have the potential to substitute the existing petroleum-based hazardous plastics (Zhang et al., 2021c). This huge potential can be ascribed to the similar thermal, mechanical, and other physicochemical properties of those conventional polymers. PLA and PBS are synthesized by the polymerization of lactic acid and succinic acid monomers. On the other hand, Polyhydroxyalkanoates (PHA) are produced by several bacterial strains through natural biosynthesis pathways (Urbanek et al., 2020).

4.6.1. Polyhydroxyalkanoates

First reported by Lemogine in 1926, PHA is synthesized by several different bacterial strains (Anderson and Dawes, 1990). PHA is primarily used by microorganisms as a stress survival mechanism. During stress conditions (nutrient scarcity, extensive heat, ultraviolet irradiations, and osmotic shock), bacteria use PHA as a carbon and energy storage reservoir (Yadav et al., 2021). It is also reported that microorganisms start accumulating PHA in excess carbon conditions however, several bacterial strains do not require such a trigger and accumulate PHA in form of intracellular granules under normal conditions. PHA can be found in different forms and structures. According to literature reports, so far around 150 different PHA structures have been documented (Mitra et al., 2020). Based on structure (number of carbons in monomeric chains), PHAs can be divided into two classes i.e., 1) PHAs comprised of short-chain lengths with 3–5 carbons (*scl*-PHAs) and 2) PHAs comprised of medium chain length with 6–14 carbon atoms (mcl-PHAs). The biosynthesis pathways of PHAs by microorganisms are well explained in many review articles (Kourmentza et al., 2017; Sharma et al., 2021; Tan et al., 2014). Thanks to their degradability, biocompatibility, and non-toxicity, PHAs can be used in different high-value-added applications such as drug delivery, tissue engineering, surgical devices, and implants (Samrot et al., 2021). However, commercial production and utilization on an industrial scale are still facing obstacles due to the high cost of production. The main reasons behind the high cost of production includes high price of glucose, discourteous batch productions, need for solvents in large amounts, and high labor costs. PHAs are also among the strong candidates for replacing petroleum-based plastics in food packaging. PHAs films/coatings have been largely investigated as a packaging material (Table 4).

As discussed earlier, PHAs can be a suitable material for packaging and paper coating if the production costs are reduced. It is a flexible polymer that can be tuned according to the need of the end application. For example, the level of crystallinity can range from 0 (flexible) to 60 % (highly crystalline), thermal properties such as *Tg* can be −52 to 4 °C, and thermal stability can range from 227 to 256 °C. The mechanical attributes such as the young Modulus of PHAs can be 3.5×10^3 MPa (rigid *scl*-PHAs) to 0.008 MPa (ductile mcl-PHAs). Similarly, the tensile strength and elongation at break can range from 8.8 to 10^4 MPa and 2 % to 1000 % respectively (Chanprateep, 2010; Chen, 2010; Cherpinski et al., 2018a; Israni and Shivakumar, 2019; Rai et al., 2011).

4.6.2. Polybutylene succinates

PBS is known as an aliphatic polyester made up of long repeating units of hydrocarbon units. The presence of these hydrocarbons over the structure of PBS provides structural flexibility (Su et al., 2019). PBS is synthesized by the polycondensation of succinic acid and 1,4-butanediol (BDO). PBS has thermoplastic processibility and balanced thermal and mechanical performance compared to other common plastics such as PLA (LACEA), PP (MA210), HDPE, and LDPE. PBS shows almost similar glass transition temperature (low *Tg*) and mechanical properties (high elongation at break; >500 %) to polyolefins. PBS is a crystalline polymer, and the degree of crystallinity defines the young's modulus (300 to 500 MPa) (Aliotta et al., 2022). The mechanical and thermal properties of PBS can be redesigned by copolymerizing PBS with other comonomer units (adipic acid, terephthalic acid, methyl succinic acid, benzyl succinic acid, and ethylene glycol) (Aliotta et al., 2022). This random copolymerization is an efficient strategy to get PBS with low melting points and a lower degree of crystallinity. Additionally, distortion temperature and tensile strength can be lowered by using the approach of random copolymerization. On the contrary, the resulting PBS after copolymerization shows higher elongation at break and impact strength (with exception of poly (butylene succinate-*co*-butylene fumarate)) (Barletta and Puopolo, 2020). PBS is degradable in soil and activates sludge, water, and compost. The rate of biodegradability is higher in water having enzymes like lipase than in water without any enzymes. Like thermal and mechanical properties, the biodegradation rate is also influenced by the degree of crystallinity of PBS. Additionally, the specimen size and condensed state have a vital role in defining the rate of PBS biodegradation (Phua et al., 2012).

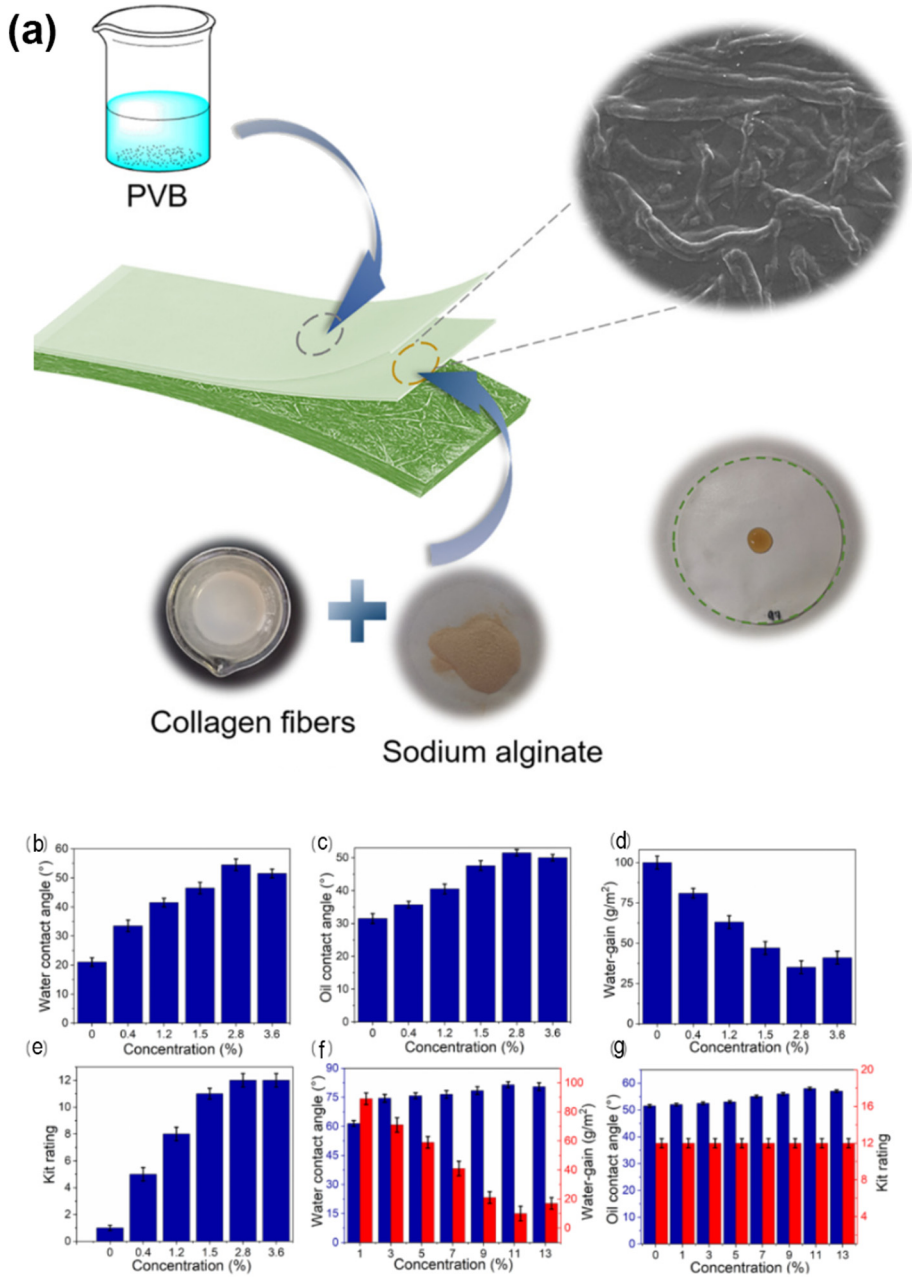

Fig. 7. a) Multilayer sodium alginate/collagen fiber barrier coating for filter paper; b, c, d, e, f, and g) barrier properties of filter paper after coating with sodium alginate and collagen fibers.
Adapted and reprinted from (Jing et al., 2022) with the permission of Elsevier.

PBS is also among the strong candidates for replacing petroleum-based plastics in food packaging. PBS films/coatings have been largely investigated as a packaging material (Table 4).

4.6.3. Poly(lactic acid)

Poly(lactic acid) (PLA) is among the most researched polyester, with numerous applications in different areas such as medicine and packaging. PLA is getting all this attention due to its biodegradability, biocompatibility, renewability (isolated from corn, wheat, or rice), recyclability, and compostable (Farah et al., 2016a). As it is known that recently, the rising environmental and economic challenges due to the use of petroleum-based packaging plastics have incited researchers and industries to replace them with biobased plastics (Cheng et al., 2009). In this regard, PLA offers numerous advantageous properties over conventional petroleum-based plastic, such as biocompatibility, biodegradability, and higher mechanical strength (Mukherjee and Kao, 2011). PLA is a thermoplastic and making its processibility even more convenient for obtaining molded shapes, fibers, and films. In 1932, Carothers (at DuPont) reported the first synthesis of a low molecular weight PLA by heating lactic acid under a vacuum by removing the condensed water (Avinc and Khoddami, 2009). The problem of low molecular weight products was resolved by introducing the ring-opening polymerization of the lactic acid approach (Huang et al., 2005).

The monomer of PLA, lactic acid can be produced by sugar conversion from vegetables, corn, and rice. Sugar conversion can be conducted through a fermentation petrochemical approach. The petrochemical approach results in an inactive form consisting of 50/50 L- and D-lactic acid. Lactic acid has two optical isomer forms known as L- and D-lactic acid. L-lactic acid rotates in a clockwise manner around the polarized light while the D-lactic acid rotates anti-clockwise (More et al., 2022). Stereochemical attributes of lactic acid define the final polymeric properties of PLA.

Table 4
Barrier properties of PLAs, PBSs, and PHAs and their composites.

Polyester	Formulations	Barrier properties		Other important outcomes	Reference
		Oxygen permeability	Water barrier		
PLA	PLA with 5 % epoxidized karanja oil	Increased from 20.9 ± 0.9 to 25.4 ± 1.2 (cm^3 mm m^{-2} day^{-1})	Increased from 71.2 ± 1.0 to 74.1 ± 0.7 (θ_w)	The incorporation of karanja oil (5–10 %) decreased the glass transition temperature and increased the elongation at break.	(Garcia-Garcia et al., 2020)
	PLA films incorporated with zinc nanoparticles (0.5 wt%)	–	Decreased by 30.5 % from 3.11 × 10^{-11} to 2.16 × 10–11 g m/m^2·Pa·s	The tensile strength increased by 30.5 %. The composite film has good antimicrobial properties against food-borne pathogens.	(Shankar et al., 2018)
	PLA films incorporated with TEMPO-oxidized cellulose nanofibrils	Decreased from 355 for neat PLA to 8.4 mL·m^{-2}·d^{-1}	–	Incorporating TEMPO-oxidized cellulose significantly reduced oxygen permeability. Mechanical properties were also	(Wu et al., 2017)
	PLA/PBS multinanolayer films	Improved up to 30 % for oxygen and 70 % for CO_2	The water barrier was improved by 40 %.	Homogenous films were obtained by monolayer coextrusion with good barrier properties against oxygen, water, and CO_2.	(Messin et al., 2020)
	PLA-starch (silane doped) bilayer	–	Improved from 31.69 ± 0.4 × 10^{-7} g s^{-1} m^{-1} to 14.26 ± 0.3 × 10^{-7} g s^{-1} m^{-1}	PLA enhanced biodegradation from 9.30 % to 5.08 %. Besides, the elongation at break was enhanced to 21.94 ± 9.48.	(Gürler et al., 2021)
	Graphene oxide reinforced composite films (2 wt%)	Decreased from 1.45 × 10^{-14} to 1.05 × 10^{-14} [kg m (m^2 s Pa)]	Decreased from 3.42 × 10^{-18} to 2.18 × 10^{-18} [kg m (m^2 s Pa)]	With the addition of graphene oxide, glass transition temperature, crystallization temperature, and elongation at the break of the composite PLA films were significantly changed.	(Ahmed et al., 2021b)
	PLA-wheat gluten protein-PLA multilayer films	Barrier properties against oxygen were enhanced 20 times (or 2000 %)	Water vapor barrier properties were enhanced ~by 20 %	The incorporation of wheat gluten into PLA followed by corona treatment significantly enhances the barrier properties of the final product.	(Rocca-Smith et al., 2019)
	PLA-clay composite films (Modification with 18-crown-6 (18C6Hec))	Oxygen permeability was reduced from 17,775 cm^3 μm m^{-2} day^{-1} atm^{-1}, which was reduced by 99.3 % to 124 cm^3 μm m^{-2} day^{-1} atm^{-1}	Swelling properties in freshwater were decreased.	Clay incorporation into PLA composite films enhances degradability. Besides, the oxygen barrier properties were significantly improved.	(Timmins et al., n.d.)
	PLA films incorporated with cinnamic acid (CA) (3 wt%)	Decreased from 187 ± 8 to 141 ± 2 × 10^{14}·cm^3/m·s·Pa.	Decreased from 0.28 ± 0.06 to 0.18 ± 0.11 g·mm/kPa·h·m^2	The addition of CA reduced the stiffness of films and enhanced the resistance to breaking. Barrier properties were significantly enhanced.	(Ordoñez et al., 2022)
PBS	PBS/Graphene Nanoplatelets composite films (0 to 1.35 wt%)	Dioxygen permeability barrier properties were increased by 35 %.	Water permeability barrier properties were enhanced by 38 %.	Graphene nanoplatelets enhanced the barrier and slightly the mechanical properties of the PBS composite film.	(Cosquer et al., 2021)
	PBS blend films with Poly (butylene adipate-*co*-terephthalate) (PBAT) and linear low-density polyethylene (LLDPE)	Significantly reduced in films containing PBS	1.5 g.mm/m^2·d·k·Pa	Films with higher content of PBS enhanced oxygen permeability and delayed fungal growth in packaging increasing the shelf life of bread.	(Bumbudsanpharoke et al., 2022)
	PBS films blended with tapioca starch (TPS) and bio-master silver (BM) (1.5–3 wt%)	Decreased the OP from 28.650 to 17.420 cm^3 μm/m^2 s Pa.	Increased from 90.170 to 95.400 g μm/m^2 with the incorporation of TPS	Minor pore size structures with high barrier property for gas permeability were attained for films containing PBS/TPS/BM films	(Aziman et al., 2021)
	PBS composite films with lactic acid through "slit die extrusion–stretching–woven compression molding.	Gas permeability of composite films decreased significantly i.e., >63 % reduction in PO_2 from 5.8 × 10^{-15} to 2.1 × 10^{-15} cm^3 cm^{-2} s^{-1} Pa^{-1}.	–	The incorporation of PLA created a network around the PBS fibers. This network of PLA contributed to the enhancement of gas barrier properties.	(Zhou et al., 2016)
	PLA-PBS films (10 and 20 wt %)/confined flacking technique was used to produce the films.	Decrease the oxygen permeability by 87 % i.e., from 1.4 to 0.6 × 10^{-14} cm^3·cm·cm^{-2}·s^{-1}·Pa^{-1}	–	The incorporation of PBS into PLA films through the confined flacking technique significantly enhanced the barrier and mechanical properties of the films.	(Xie et al., 2015)
	PBS/poly (butylene adipate-co-terephthalate films (containing 25 %, 50 % and 75 % PBS (w/w))).	Oxygen permeability decreased from 4.41 ± 0.01 to 0.68 ± 0.01 × 10^{16} mol/m^{-1}·s^{-1}·Pa^{-1}.	Water vapor permeability decreased from 7.09 ± 0.08 to 2.90 ± 0.02 × 10^{-12} mol/m s Pa.	Blending PBS at 25 % revealed a significant enhancement in the mechanical properties of the films. Films with 75 % of PBS revealed good barrier properties.	(de Matos Costa et al., 2020)
	Banana starch nanocrystals/poly (butylene succinate) bio-nano composite packaging films.	Oxygen permeability decreased from 560.3 cc m^{-2} day to 216.3 cc m^{-2} day	Water vapor permeability decreased from 114.5 to 54.1 g m^{-2} day.	The incorporation of PBS significantly contributed to the mechanical properties of the composite films. Elongation at break has been increased from 1 % to 51 %.	(Saeng-on and Aht-Ong, 2018)
PHA	Thermoplastic corn starch-based films containing bacterial cellulose/PHA	Oxygen permeability decreased from 42.3 to 2.86 × 10^{-18} m^3·m·Pa^{-1}·s^{-1}·m^{-2}	Water vapor permeability decreased from 15.52 to 6.42 ± 0.02 × 10^{-13} Kg·m·Pa^{-1}·s^{-1}·m^{-2}	The barrier properties of corn starch-bacterial cellulose have significantly improved by incorporating electrospun PHB fibers. The best results were obtained for the films containing 15 wt% bacterial cellulose nanowhiskers and PHB.	(Fabra et al., 2016a)
	Tri-layered wheat gluten and electrospun PHA films	Oxygen permeability decreased from 15.10 ± 2.42 to 4.36 × 10^{-15} m^3·m·Pa^{-1}·s^{-1}·m^{-2}	Water vapor permeability decreased from 16.02 ± 0.43 to 3.11 ± 0.64 × 10^{-11} Kg·m·Pa^{-1}·s^{-1}·m^{-2}	The barrier performance of wheat gluten-based films has been enhanced by incorporating electrospun PHA fibers. This layered structure significantly enhanced the barrier preference of the films.	(Fabra et al., 2015)

Table 4 (*continued*)

Polyester	Formulations	Barrier properties		Other important outcomes	Reference
		Oxygen permeability	Water barrier		
	Multilayered PHAs based films with cellulose nanocrystals	–	Water vapor permeability decreased from 3.22 ± 0.12 to 0.87 ± 0.92 × 10^{-11} kg·m^{-2}·Pa^{-1}·s^{-1}	The multilayered films revealed good transparency, interlayer adhesion intermediate mechanical performance, and significantly improved water barrier properties.	(Figueroa-Lopez et al., 2020)
	PHAs with a nano keratin additive	Oxygen permeability decreased from 1.75 ± 0.25 to 0.90 ± 0.05 × 10^{-19} m^3·m·Pa^{-1}·s^{-1}·m^{-2}.	Water vapor permeability was significantly reduced from 3.54 ± 0.40 to 1.22 ± 0.10 × 10^{-14} kg m s^{-1} m^{-2} Pa^{-1}.	The barrier properties were enhanced significantly depending on the grade of PHA used in the nanocomposite. Additionally, good adhesion was another factor that resulted in good barrier properties.	(Fabra et al., 2016b)
	PHA-PBAT-CNC multilayer films	Oxygen permeability decreased from 57.81 ± 21.45 to 1.12 ± 0.61 × 10^{-19} m^3·m·Pa^{-1}·s^{-1}·m^{-2}.	Water vapor permeability was significantly reduced from 11.47 ± 0.06 to 0.82 ± 0.03 × 10^{-11} kg m s^{-1} m^{-2} Pa^{-1}.	The resultant films revealed improved adhesion, transparency, and barrier properties. 1 μm layer of CNC in a multilayer film system was enough to reduce the oxygen permeability between 71 % and 86 %.	(Melendez-Rodriguez et al., 2021)

Nowadays, PLA can be obtained in different lengths by using different available approaches (polycondensation, ring-opening and enzymatic polymerization, and azeotropic dehydration) (Garlotta, 2001). However, it is worth noting that none of these available methodologies are simple/easy to execute. The production of PLA requires controlled conditions for temperature, pH, and pressure, a catalyst, and prolonged polymerization periods. On a commercial scale, PLA is obtained through the ring-opening polymerization approach (Fournier et al., 2022). PLA exhibits better thermal processibility compared to PHA, poly(ethylene glycol) (PEG), and poly(γ-caprolactone) (PCL), thus requiring less energy (25 %–55 %) for making films or fibers. Less energy requirement makes PLA a cost-effective biobased polymer that enhances its application areas (Rajeshkumar et al., 2021). The degradability of PLA depends upon the crystallinity molecular weight and morphology. PLA is also among the strong candidates for replacing petroleum-based plastics in food packaging (Qiu et al., 2021b). PLA films have been largely investigated as a packaging material (Table 4).

PLA exhibits good barrier properties against gas and WVTR. Gas permeation properties of PLA and PLA composite films have been reported by different researchers (Aversa et al., 2020; Ebadi-Dehaghani et al., 2015; Pinto et al., 2013; Qiu et al., 2021a). Altering the ratio of L- and D-lactic acid influences the crystallinity of the final films. Films with lower higher crystallinity displayed a good barrier again gas permeation. Additionally, an increase in crystallinity also influences the WVTR rate of PLA films. Films with higher crystallinity show lower WVTR than films with lower crystallinity values (Farah et al., 2016b).

5. Concluding remarks and future perspective

Industries are concentrating on creating various biobased or biodegradable alternatives utilizing renewable resources to totally or partially replace petroleum-based plastic packaging materials. Despite all of the current knowledge in sustainable packaging, bioplastics still lack key physicochemical and biological properties that are impeding their adoption in industry. Technological breakthroughs in the field of bioplastic production and application are fast growing, creating new opportunities for academics and industry to collaborate and develop sustainable packaging solutions. Among the major prerequisites of a good food packaging material is that; i) it should have good barrier properties against oxygen and other related gases to keep the food comedies safe and ii) it should have resistance against water. Most biopolymers have intrinsic hydrophilic properties and a good barrier against oxygen, thanks to their swelling behaviors upon contact with moisture. It is, therefore, necessary to explore green routes for enhancing the hydrophobic properties of biopolymers such as cellulose, chitosan, starch, and alginate. Currently, available approaches such as multilayer coating of nanocomposites can be further enhanced by designing them in a more systemic way to achieve the maximum desired results (barrier properties). Modified nanocellulose and lignin nanoparticles are among the prime future candidates for making nanocomposite-based packaging films. Other potential polymers include nonpolar biopolymers such as PLA, PHB, PHA, and PHBV, with good water vapor permeability values. The growing market of biobased/biodegradable polyesters for packaging films is an indicator of its great potential as a packaging material. Functional nanoparticles of biopolymers are widely developed and used majorly for medical applications, but there are very few literature reports regarding structured nanoparticles for paper/cardboard coating. In addition to multicoating approaches, converting biopolymers such as chitosan, alginate, and zein into structured nanoparticles for barrier applications in cardboard coating is another unexplored arena. These polymers offer the desired structural flexibility for easy tuning the properties making them easy to process for coating applications. Considering the literature reports, it can be stated that biobased alternatives are available to every fossil-based product that is been used in the packaging industry, however, all these biobased products have serious problems with quantities, renewability, and cost-effectiveness. Other than first-generation biomass, lignocellulose from agricultural waste and other types of biowastes offers a renewable feedstock to produce sustainable and biobased packaging materials. The production of such feedstock from agricultural waste can become more efficient if the efficiencies of biorefinery processes are optimized towards industrial needs i.e., less energy and labor-intensive.

The form of coating solution and type of substrate is also emerging as influencing factor in the overall application and marketability of biobased coating solutions. Both liquid and solid coatings come with their advantages and disadvantages. For example, solid coatings offer tailored wettability, resilience against thermal degradation, and tunable viscosity. However, the use of harsh solvents and inhomogeneous dispersibility made liquid coatings unfavorable in many applications. As an example, the production and application of liquid coating solutions based on chitin/chitosan, cellulose, and cutin are at a more technological readiness level compared to solid coatings (Gigante et al., 2021). Similarly, solid coatings are solvent-free with good dispersing ability making them more cost-effective compared to liquid coatings. However, the risk of thermal degradation and possible low adhesion towards many substrates limits their application areas.

CRediT authorship contribution statement

Muhammad Mujtaba: Investigation, Conceptualization, Writing - Original draft; Juha Lipponen: Supervision, Funding acquisition, Mari Ojanen: Reviewing and Editing; Sami Puttonen: Reviewing and Editing, Henri Vaittinen: Conceptualization, Reviewing and Editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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