



Thermal Properties of Biopolymer Films: Insights for Sustainable Food Packaging Applications

Yasir Abbas Shah¹ · Saurabh Bhatia^{1,7} · Ahmed Al-Harrasi¹ · Fatih Oz² · Mujahid Hassan Khan³ · Swarup Roy⁴ · Tuba Esatbeyoglu⁵ · Anubhav Pratap-Singh⁶

Received: 13 December 2023 / Accepted: 24 June 2024

© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2024

Abstract

Poor thermal stability of packaging materials represents a significant obstacle impeding their applications as alternatives to non-biodegradable plastics in the food packaging sector. The thermal stability of biopolymeric films is essential for upholding their structural integrity and preventing degradation at different temperatures during processing, transportation, and storage, thereby safeguarding the quality and safety of packaged food items. A deeper understanding of the interplay between material composition, processing conditions, and thermal behavior will foster the development of stable edible films capable of withstanding elevated temperatures while maintaining their structural integrity and functional attributes. This review provides an overview of various thermal analysis techniques available for analyzing biodegradable edible films (viz. Differential Scanning Calorimetry, Thermogravimetric Analysis, Dynamic Mechanical Analysis, and Thermomechanical Analysis), as well as explores the interrelation between film properties and thermal stability such as film crystallinity, morphological attributes, chemical arrangement, nano-reinforcements and interaction with other ingredients. Furthermore, the thermal behaviour of biopolymers and the recent advancements aimed at engineering desirable thermal behaviour into edible films are extensively discussed. The present study contributes to the current knowledge base and serves as a valuable resource for researchers in the field of food packaging and material science.

Keywords Food Packaging · Edible Films · Thermal Stability · Biopolymers · Bioactive Compounds

✉ Saurabh Bhatia
sbsaurabhhatia@gmail.com

¹ Natural and Medical Sciences Research Center, University of Nizwa, Birkat Al Mauz, Nizwa 616P.O. Box 33, Oman

² Department of Food Engineering, Faculty of Agriculture, , Ataturk University, 25240 Erzurum, Türkiye

³ Department of Bioscience and Agro-Food and Environment Technology, University of Teramo, Teramo 64100, Italy

⁴ Department of Food Technology and Nutrition, School of Agriculture, Lovely Professional University, Phagwara 144411, Punjab, India

⁵ Department of Molecular Food Chemistry and Food Development, Institute of Food and One Health, Gottfried Wilhelm Leibniz University Hannover, 30167 Hannover, Germany

⁶ Faculty of Land & Food Systems, BC Food and Beverage Innovation Centre, The University of British Columbia, 2205 East Mall, Vancouver BC-V6T2G2, Canada

⁷ School of Health Sciences, University of Petroleum and Energy Studies, Dehradun, Uttarakhand, India

Introduction

A significant quantity of non-biodegradable plastic is discarded into the natural surroundings, resulting in serious environmental contamination. The development of biodegradable edible films has emerged as a means of reducing the use of synthetic or non-biodegradable plastic and preserving the environment [1]. Carbohydrates, protein, and lipids have been used to fabricate edible films individually or in combination with each other. Thermal stability is an important property for edible films, as it ensures that the film maintains its structural integrity and does not break down or degrade when exposed to high temperatures (Bhatia, Al-Harrasi, Shah, Altoubi, et al., [2]). To ensure the effectiveness of edible films as packaging materials, it is necessary to consider their thermal stability during the development and formulation of the films. There are different methods used to evaluate the thermal integrity of edible films such as Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Dynamic Mechanical Analysis (DMA),

and Thermomechanical Analysis (TMA). Thermo-physical properties such as thermal conductivity, diffusivity, glass transition behaviour, crystallization temperature, melting temperature, decomposition temperature, heat deformation temperature and heat expansion rate play an important role in determining the stability of the food packaging material. Ideally food packaging material must have poor thermal conductivity like plastics to restrict the heat transfer from packaging material to food [3].

Food packaging materials like plastics do not contain free electrons when compared with metallic packaging material, and thus restrict the transfer of heat from the environment to packed food products. Due to the recent advancements in food packaging materials, biomaterials derived from starch and other sources showed drastic improvement in mechanical strength and color attributes. Nevertheless, most of the biopolymers used in food packaging lack thermal insulation properties like synthesized plastic [4]. Most of the plastic materials used in the food packaging industry show intermediate thermal conductivity (0.15–0.4 W/mK) [5]. The addition of bioactive compounds to edible films can affect their thermal properties [6]. This review focuses on the thermal properties of edible films and various thermal analysis techniques available for analyzing biopolymeric films. Furthermore, the current review article explores the interrelation between film properties and thermal stability such as film crystallinity, morphological attributes, chemical arrangement, nano-reinforcements and interaction with other ingredients.

Methods to Determine the Thermal Stability of Edible Films

The thermal properties of edible films determine their stability during storage and transport. Temperature changes can cause the film to lose its mechanical and barrier properties, leading to spoilage of the food product. The thermal properties of edible films are also important for optimizing processing conditions. The commonly used methods to analyze the thermal properties of edible films are TGA, DSC, DMA, and TMA.

Thermal Gravimetric Analysis (TGA)

TGA is a valuable technique for assessing the thermal stability of films at higher temperatures (around 600 °C). This is one of the main features of packaging materials as they may be exposed to higher temperatures in packaging procedures such as sealing. In addition, TGA also helps in determining the effect of any additive or process condition or any other variable on the blank polymeric material especially

polymeric degradation [7]. To differentiate the thermal stability of different films in terms of their decomposition or weight loss it is important to record their decomposition stages at a constant heating rate under an inert atmosphere by using TGA. Generally, the first weight loss during TGA analysis of edible films is observed due to the presence of free and bound water vapors whereas the second, as well as third stages of weight loss, corresponding to the decomposition of plasticizers such as glycerol and polymer [8]. It is important to compare the percentage of weight loss in each stage of control (blank polymer films) with composite films to understand the effect of secondary polymer or any additives on the thermal stability of the films. Additionally, the thermal attributes of the films such as initial degradation (Tonset), maximum decomposition (Tmax) and the residual mass left at the highest temperature (Tmrs) during TGA analysis must be evaluated [9]. A number of analyses can be carried out on the data obtained from the TGA using various methods. Some of the factors that affect this data are sample mass, heating rate, gas flow rate and nature, and the mathematical procedure that is applied to validate the data [10]. Reaction rate describes the derivative of the conversion, (α) with respect to time. The TG curves can be used to calculate the value of (α) in terms of mass loss using the following equation [10].

$$\alpha = \frac{m_o - m}{m_o - m_\infty} \quad (1)$$

In this equation, m represents the measured mass of a given sample at temperature T , m_o indicates the initial mass while m_∞ is the mass at the end of the non-isothermal TGA analysis.

The thermal stability of the film containing a single polymer is considered as control and its decomposition stages are usually compared with composite films to understand the effect of additives such as polymer, bioactive compound, plasticizer, surfactant, etc. on the control film (Table 1). Several examples of control film containing single polymers, those are widely used in edible films are highlighted in Table 1.

DSC (Differential Scanning Colorimetry) Analysis

DSC is generally used to examine characteristic temperatures, corresponding phase change enthalpies, crystallization behaviour and most importantly glass transition by identifying the change in heat capacity over the two periods [24]. Recently more sensitive techniques like modulated DSC (MDSC) have been employed to enhance the efficiency and precision of intricate thermal events in the study of edible films. Methods such as TMA, DMA and

Table 1 Thermal decomposition of films containing single polymer

Biopolymers (considered control)	First stage	Second stage	Third stage	References
Chitosan	100 to 200 °C, attributed to water evaporation	At temperatures ranging from 200 to 400 °C, the second stage of decomposition occurred attributed to the disintegration of chitosan resulting from glycosidic ring dehydration and the breakdown of its molecular chains., Tmax was observed close to approximately 290 °C to 300 °C.	No third stage	[11]
	50–100 °C (5% decomposition due to evaporation of loosely bound water)	270–320 °C due to decomposition of chitosan	No third stage	[12]
Sodium alginate	160 °C with a weight loss of about 6.5%	95–340 °C due to saccharide ring dehydration and the subsequent breakage of the biopolymer's primary chain.	340 °C onwards due to the decomposition of the polymer	[13]
	50–192 °C (17.5% mass loss)	The temperature range reported was 192 °C to 486 °C, maximum deterioration occurred at 246 °C, resulting in a substantial 44% reduction in mass due to the breakdown of glycosidic bonds, the loss of hydroxyl groups, and the evolution of carbon dioxide (CO ₂)	No third stage	[14]
k-Carrageenan	59–88 °C due to evaporation of free water	214–232 °C Tonset and Tmax were 214.37 and 226.51 °C	No third stage	[15]
	30 to 90 °C was due to evaporation of the water	Temperature range 130–220 °C, attributed to the degradation of the glycerol	210–250 °C, due to thermal degradation of carrageenan matrix	[16]
Gelatin	Range 60–120 °C; due to the evaporation of water.	170–230 °C due to the presence of the glycerol	230–330 °C due to polysaccharide decomposition	[17]
	A 5.4% reduction in weight caused by the evaporation of water	120–600 °C with weight loss of around 89.26% due to degradation of large-size or biopolymer fragments	No third stage	[18]
Fish skin gelatin	In the range of 23–176 °C, attributed to the evaporation of water	192–426 °C, attributed to the degradation of the fractions of protein with a lower molecular weight	429–456 °C attributed to the degradation of the fractions of protein with lower molecular weight	[19]
Pectin	50–100 °C was attributed to the evaporation of water	200–320 °C (Tmax: 240 °C), was attributed to the decomposition of the pectin chain; pectin control film showed the Tg value: 220.84 °C	305 °C to the decomposition of the pectin chain	[20]
Citrus pectin	Release of free water up to 100 °C, with 6% weight loss	100 and 180 °C, with 8% weight loss	180 and 350 °C, due to degradation of polymer with weight loss of 64%	[21]
Whey protein	40–135 °C; Tmax 71 °C	135–450 °C; Tmax: 303 °C	450–560 °C Weight loss was 5.2%	[22]
Cellulose	20–100 °C with weight loss 12.6%	Tmax: 238 °C	Residues primarily composed of carbonaceous material persisted after thermal processing at temperatures as high as 500 °C.	[23]

oscillation techniques are not employed commonly as they possess greater sensitivity [25]. Recently MDSC analysis was used to determine very low Tg temperatures ranging from about –22 to about –39 °C [26]. DSC thermograms of films made up of natural semi-crystalline polymers help in the determination of glass transition temperatures (Tg), melting temperatures (Tm), crystallization temperatures, crystallinity, and enthalpies (ΔH) [27]. Enthalpies of transitions can be determined using the DSC curve by integrating the peak corresponding to a particular thermal event [28,

29]. For a specific transition, the enthalpy can be described using Eq. 2:

$$\Delta H = KA \quad (2)$$

In this equation, ΔH indicated the enthalpy of transition, K represents the calorimetric constant, and A is the area under the peak.

Glass transition of polymeric material is related to the change of molecular mobility of the polymer due to rise in

the temperature. This physical shift of polymeric material from glassy to an amorphous state impacts the molecular motion of polymeric material and thus controls thermal, mechanical and barrier properties [30]. It was suggested that the changes in the T_g , T_m and ΔH are the potential markers in determining the compatibility between several biopolymers [31]. DSC overlay of edible films generally presents both endothermic (water evaporation, melting, polymer degradation and glass transitions) and exothermic peaks (crystallization) (Fig. 1).

DSC is probably not a suitable approach for the thermal stability assessment of composite or complex materials such as edible films made of two polymers with bioactive components. This is due to the formation of multiple exothermic or endothermic peaks in both heating and cooling cycles while analyzing composite materials [32]. This makes the thermogram complicated in terms of distinguishing the T_g peak, as the endothermic relaxation enthalpy is descriptive for polymeric materials in the glassy state that experiences natural ageing. The endothermic peak in the DSC thermogram also represents melting temperature (T_m), and one or more glass transitions, that further complicate the thermogram in identifying peaks corresponding to T_m and T_g . Crystallization is an exothermic process and the degree of crystallinity of the edible films can be calculated from

the area of the exothermic peak (further conformed from XRD of the same sample) [33]. In the majority of the composite edible film studies, the DSC thermogram of control (generally thermogram of single polymer without additive) was compared to the thermogram of composite material to understand the changes in the thermal stability of composite material (Table 2).

Dynamic Mechanical Analysis (DMA)

The DMA technique is extensively employed in the characterization of a material's properties with respect to various parameters such as temperature, time, frequency, stress, atmosphere, or a combination of these parameters [52]. Polymers exhibit two distinct responses to the energy of motion, namely elastic response, which is crucial for shape recovery, and viscous response, which plays a vital role in dispersing mechanical energy and preventing breakage. The viscoelastic properties, which refer to the responses of a material, are analyzed through the utilization of dynamic mechanical analysis (DMA) while subjecting the material to low levels of mechanical force. The viscoelastic behaviour of polymers is dependent upon the variables of temperature and time [53]. DMA instruments are equipped with regulated heating and cooling mechanisms to investigate

Fig. 1 General DSC overlay of edible films (tm: melting temperature; tc: crystallization temperature; tg: glass transition)

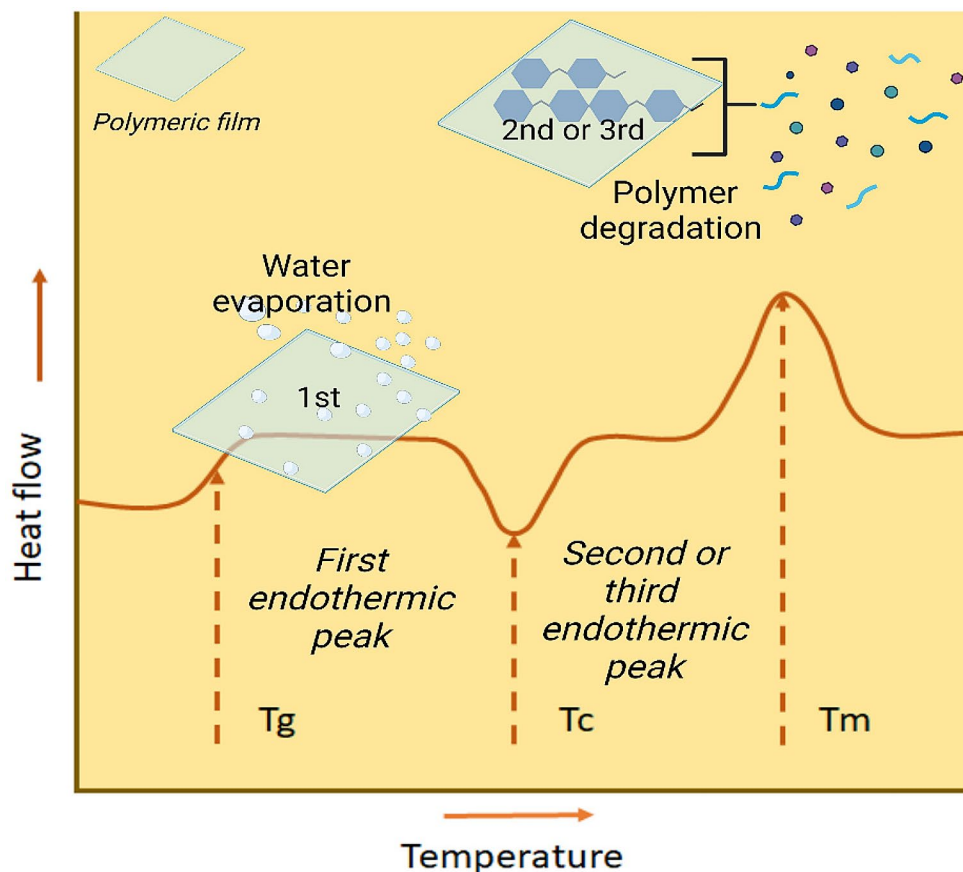


Table 2 Endothermic and exothermic peaks in DSC thermogram for the neat polymers

Biopolymer	Endothermic peak of blank	Exothermic peak of blank	References
Sodium alginate	134.39 ± 2.64 °C due to melting of polymer	211.94 ± 1.42 °C; due to decomposition of polymer	[26]
Pectin	154 °C 84.67 due to loss of adsorbed and structural water	229.82 (decomposition of pectin)	[34] [35, 36]
Sodium caseinate	Tg reported in three studies: 73.4 °C, 75.57 °C, 78 °C		[37]
High methoxyl pectin	Tg -6.32 °C		
Chitosan	Two endothermic peaks (72.24 and 154.64 °C) 60–100 °C due to water evaporation (peak temp: 80 °C)	269.65 °C due to chitosan degradation. Second endothermic peak Tg: 166 °C; third exothermic peak Tc: 275 °C	[38]) [39])
Gelatin film	82.0 °C, attributed to the melting of gelatin crystal structure.		[40]
Guar gum	106 °C (Tg) and 254 °C; attributed to the thermal decomposition of the guar gum	305 °C (due to the thermal degradation of the polymer)	[41]
Gelatin (different grades)	Tg = 51–59 °C; 80–82.5 °C (denaturation temperature)		[42]
Gelatin (pigskin gelatin: type A)	Tg = 57.5 ± 1 °C		[43]
Gelatin from bovine skin (Type B)	71.8 °C; due to the evaporation of water	222.7 °C; due to the breakage of the gelatin chains.	[44]
Poly(vinyl alcohol)	Tg = 26.3 ± 1 °C		[43]
Bovine gelatin	Tg (°C): 22.3; Tmax: 82.0; delta H (J/g): 14.4		[45]
Cold water fish skin gelatin	108–114 °C may be attributed to different processes such as evaporation, recrystallization of small gelatin crystallites or glass transition of amino acids.	261–263 °C due to polymer degradation	[46]
Pure poly (lactic acid)	Tg: 55 °C and an endothermic peak at about 108 °C.	Tc: 108.4 °C; Tc: 166.7 °C.	[47]
Poly(lactic acid)	Tg: 51.4 °C	Tc: 109.8 °C; Tm: 169.9 °C	[48]
Cellulose	The temperature range for endothermic peaks is between 50 and 150 °C; the first endothermic peak could be attributed to the evaporation of water molecules	The second endothermic peak is a result of the breakdown of hemicellulose, the depolymerization process of cellulose, and the third decomposition stage involving the components of lignin and α-cellulose, by an exothermic peak.	[33]
Wheat gluten protein	88 °C due to denaturation		[49]
Carboxymethyl cellulose	Tg: 99.6 °C		[50]
Tara gum with glycerol	Tg: 52 °C		[51]

the impact of temperature on the stiffness and resiliency of polymers [54]. The dynamic mechanical analysis method is a versatile approach that can be used to simultaneously characterize the rheological and thermal properties of an extensive range of different types of samples [55]. DMA can provide a comprehensive understanding of the thermal behavior and stability of edible films by measuring their mechanical response as a function of temperature [53]. This information aids in the development, formulation, and selection of edible films with improved thermal stability for various food packaging and preservation applications.

Thermomechanical Analysis (TMA)

Thermomechanical analysis also referred to as TMA, is one of the most important tools in the field of material science,

particularly when it comes to thermal analysis. The alteration in the dimensions of the sample as a function of temperature is the basis of the TMA technique [56]. TMA is a useful technique for obtaining significant insights into the thermal expansion, glass transition temperature (Tg), softening points, composition, and phase changes of materials with varying geometries by subjecting the materials to a constant force as a function of temperature [57]. TMA can be employed to study the thermal behaviour of thin films, coatings, and surface treatments. It allows for the analysis of thermal expansion properties and the determination of the stress-strain behaviour of these thin layers. TMA can be used in optimizing the design and performance of coatings and thin films for various applications. While Dynamic Mechanical Thermal Analysis (DMTA) measures the viscoelastic properties by applying an oscillatory force.

Together, TMA and DMTA techniques offer a comprehensive understanding of a material's thermal and mechanical properties, crucial for applications like biopolymeric films in packaging.

Effect of Bioactive Compounds on the Thermal Behaviour of Edible Films

The thermal properties of a film are indicative of its ability to withstand varying temperatures and can have a significant impact on its compatibility to be employed as a food packaging material [58]. The thermal behaviour and stability of biopolymers can vary significantly depending on the specific type of biopolymer and its source. The thermal characteristics of films are frequently assessed to ascertain key parameters such as the glass transition temperature, melting point temperature and degradation temperature. These parameters serve as a viable metric for a uniform multi-polymer mixture and may be regarded as a standard for evaluating the capacity to combine polymer/biopolymer blends and withstand fluctuations in temperature [59]. Adding bioactive compounds to edible films or preparing a composite material with the addition of two or more biopolymers can have various effects on the thermal properties such as thermal stability, melting temperatures and glass transition temperatures of the resultant films [60].

Thermal properties of the pearl millet starch (PMS) and carrageenan gum (CG) based edible films were examined using DSC. The authors reported that the melting temperature (T_m) of the PMS films increased from 98 °C to 118 °C with the addition of CG due to the strong intermolecular interaction between starch and carrageenan [61]. In another study, Zhou et al. [62] studied the thermal characteristics of cassava starch-based (CS) films loaded with varying concentrations of cinnamon essential oil (CEO) using TGA. The results demonstrated that the addition of CEO in the CS-based edible films increased the thermal stability of the films due to the higher compatibility between the film-forming components including polymer and oil [62]. The impact of bioactive compounds on the thermal characteristics of edible films can vary based on factors such as the type, concentration, and compatibility of the bioactive compound with the film matrix.

The thermal properties of carrageenan, guar gum, and glycerol-based edible films containing varying concentrations (0.2%, 0.4%, and 0.6%) of lemongrass essential oil (LGO) were investigated using DSC [63]. The results of the DSC analysis of the prepared films revealed that T_g increased with increasing the concentration of oil from 0.2 to 0.6%. T_g of the edible film was determined to be 221.78°C, 237.91°C, and 241.26°C for formulations containing 0.2%,

0.4%, and 0.6% oil, respectively [63]. In a previous study, DSC analysis was carried out for the edible film based on arrowroot starch and gelatin composite incorporated with cranberry powder [64]. The thermal analysis revealed that increasing the concentration of cranberry in the films caused a decrease in the T_g range. Incorporating fruit pulps into the polymeric matrix of the film has been found to release sugars that act as plasticizers. This plasticizing effect modifies the polymer interactions, increasing the free volume, enhancing chain motility, and reducing the T_g of the film [65, 66]. Furthermore, the incorporation of different bioactive compounds and their effect on the thermal properties of edible films have been shown in Table 3.

Crystallinity and Thermal Stability of the Films

Ideally, edible films must be highly crystalline to gain more thermal stability and mechanical flexibility [60]. However, most of the natural polymers used in the preparation of edible films are semi-crystalline and approaches employed to increase polymer crystallinity generally increase the brittleness of the edible films. In addition, crystallizing polymers on an industrial scale can be very difficult. Approaches like co-crystallization to enhance the crystallinity and thermal stability of polymeric films while maintaining their mechanical flexibility could be reliable but have not been used so far. Thus, it is important to draw the relationship between the crystallinity and the thermal behaviour of the film [75]. There are multiple factors such as functional groups, molecular weight, branch degree, cross-linking, and degree of crystallinity of the polymers that impact the thermal stability of the edible films as shown in Fig. 2.

XRD (X-ray diffraction analysis) is an analytical technique used to determine the degree of crystallinity of materials. Important attributes such as the nature of crystal lattice (polymorphic), crystal structure, polymorphism, preferred crystal orientations (texture), crystal defects, percentage of crystalline material, and most importantly crystal size can be determined using XRD [76]. The percentage of crystallinity can be calculated using the Eq. 3 [77].

$$\text{Crystallinity (\%)} = \frac{\text{area under peaks}}{\text{Total area}} \quad (3)$$

With the latest advancements in XRD, small-angle, ultra-small-angle X-ray and neutron scattering approaches can be used to offer structural data on the nanometer-to-micron length scale [78]. X-ray diffractogram of amorphous-crystalline structures is usually represented by strong characteristic peaks related to the crystalline zone where narrowness

Table 3 The incorporation of bioactive compounds and their effect on the thermal properties of the edible films

Biopolymer(s)	Bioactive compounds/ Source	Plasticizer	Type of analysis	Effect on thermal properties	Refer- ence
Chitosan (2%)	Pomegranate peel extract (0.2–1 g/mL)	Glycerol (1%)	DSC	T_g temperature of film samples decreased with increasing the concentration of the extract. Overall thermal stability reduced.	[67]
Pectin (2%)	Gamma-aminobutyric acid (GABA) (5, 10, 15%)	Glycerol (10%)	DSC	T_g was 3.3 °C for the control film, but adding 5%, 10%, 15% GABA and 10% glycerol dropped T_g to 1.2 °C, -5.3 °C, -8.1 °C, and -12.7 °C, respectively. The addition of GABA lowered T_m and ΔH_m of pectin films.	[68]
Potato starch (3%)	Clove essential oil (0.5–2.5%)	Glycerol 1%	DSC	At oil concentrations up to 1.0%, ΔH_m , T_{on} , and T_m values increased. At higher levels of oil, ΔH_m , T_{on} , and T_m values decreased.	[69]
Chitosan (1%) and Sodium Alginate (3%) composite	<i>Ficus racemosa</i> aqueous fruit extract (0.5–1.5%)	Glycerol (5%)	TGA	Improved thermal stability	[70]
Gelatin (3%)	Fresh orange (<i>Citrus sinensis</i>) peel extract (5 and 10 mg/mL)	Glycerol (15%)	DSC	T_g temperature increased from 69 °C to 71.90 °C with increasing the concentration of extract.	[71]
Methylcellulose (3%)	Ethanolic extract of freeze-dried apple skin and aqueous extract of apple skin (10, 20, 25%)	N/A	DSC	When compared to the control, films containing extracts exhibited a shift to a lower T_g .	[72]
Carboxymethyl cellulose (2%) and gelatin (2%) composite	Antioxidant of bamboo leaves (0.1–0.4%)	Glycerol	DSC	T_m of the films increased with increasing the concentration antioxidant of bamboo leaves. T_m increased from 268.67 °C to 278.24 °C.	[73]
Cassava starch and chitosan	Pitanga (<i>Eugenia uniflora</i> L.) leaf extract and/or natamycin	Glycerol	TGA	The addition of pitanga leaf extract enhanced the thermal stability, as demonstrated by increased glass transition temperatures and higher maximum degradation temperatures	[74]

and broadness determine the percentage of crystallinity [79]. The most important factor that determines the crystalline behaviours is the polymer's inherent properties such as its type, source, and composition (Table 4) that ultimately impact the thermal stability of the films.

Effect of Morphology and Surface Property on the Thermal Behaviour of Edible Films

The thermal resistance of the films is also influenced by their morphology [62]. The morphology of the edible films is generally determined by scanning electron microscopy. SEM coupled with EDS offer not only morphological insights but also provide the elemental composition of the material which is essential to assess the heat insulation of the material. Also, atomic force microscopy helps in determining surface roughness of the polymeric films by calculating roughness means square values which is again an essential parameter to correlate with heat conduction. Morphological attributes such as compactness, density, porosity, cracks, uniformity, roughness and particles impact the heat conduction of the material and thus impact the overall thermal stability of the edible films. Similarly, surface hydrophobicity

and hydrophilicity also impact the thermal stability of films [88]. Surface hydrophilicity or wettability of edible films can be determined by using a goniometer to measure the contact angle of a droplet on a surface [89]. Hydrophilic material attracts more water vapors over the surface of the films resulting in variation in thermal conduction.

Thermal Behavior of Common Edible film Constituents

The low thermal conductivity of biopolymer films compared to synthetic films is one of the major technical barriers that limit its application at the commercial scale [90]. Biopolymer films are relatively more sensitive to heat than synthetic films and thus offer low thermal resistance. Therefore, improving the thermal conductivity of biopolymers and their respective composites is of great interest. To engineer high thermal conductive films using biopolymers more chemical insights are required such as polymer chain structural arrangements (backbone and side chains) and interchain coupling (hydrogen bonding and crosslinking) in the films [91]. Heat conduction expresses the transfer of heat across a material directed by a temperature gradient.

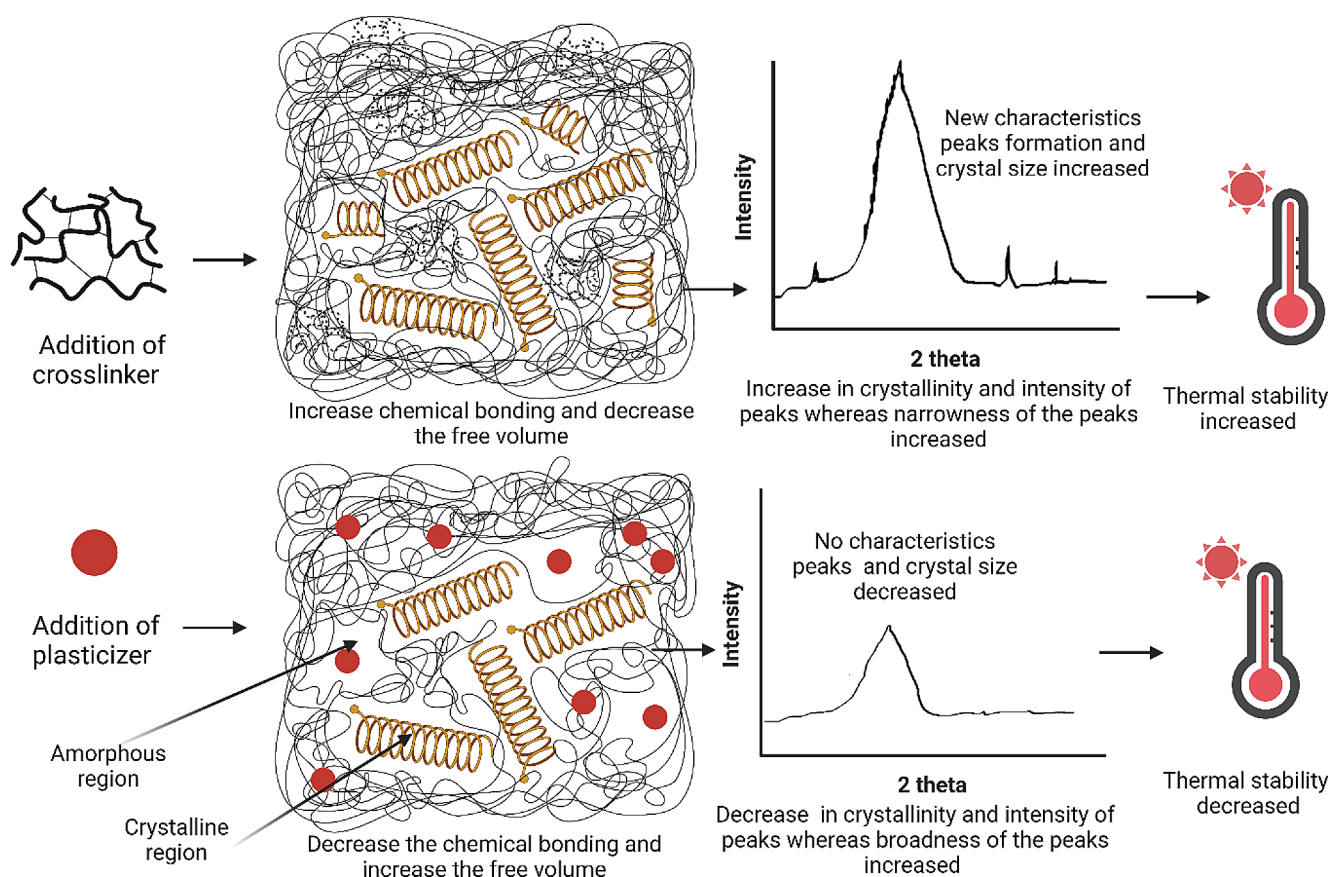


Fig. 2 A representation of the effect of additives on the crystallinity of the edible films and effecting the thermal stability

In contrast to metals, heat conduction in polymeric material occurs via lattice vibrations (phonons) [92]. Normally, an amorphous polymeric structure leads to a reduction in the normal free path of phonons, which decreases the overall heat conductivity [93].

Synthetic polymers with highly conducting or insulating features generally form toxic residues when exposed to higher temperatures. Therefore, biopolymers-based films have been considered over synthetic polymers to prevent the immigration of toxic components into food. Film composition and process conditions are critical parameters in determining the thermal stability of the films. Some films are designed in a way to bear thermal stress e.g., thermoplastic starch is fabricated by using edible starch plasticized with food-grade plasticizers to improve the overall thermal stability than native starch-based films. The type and quantity of plasticizer used in the development of thermoplastic starch-based films greatly impact their thermal stability [94].

There are various sources of starch, however, some sources provide a high yield of starch with its high amylose content. Ulluco starch-based edible films have been reported for their better thermal stability profile [95]. The chemical composition of the films in terms of the ratio of

polysaccharides, proteins and lipids also impacts the thermal stability of the films. Generally, the thermal stability of polysaccharides is poor as these macromolecules are not conducive to their successive molding processing. Using organic or synthetic crosslinkers to improve the crosslinking is considered as reliable approach to improve the thermal stability of polysaccharide-based films [91]. Although polysaccharide aerogels possess low thermal conductivity, its equivalent to silica aerogels and synthetic polystyrene foams. Thus, the incorporation of polysaccharide-based aerogels can be used to prepare films with relatively high thermal stability [96]. Likewise blending between polysaccharide and protein offers more thermal resistant films e.g., blending of collagen–alginate improved the thermal stability by 15 °C after alginate addition in neat collagen (native) materials [97].

Chitosan shows great sensitivity to several types of degradation, including thermal degradation, which is dependent on the degree of deacetylation. It is reported that commercial chitin thermally decomposed at lower temperatures than highly deacetylated chitosan [98]. The blending of neat chitosan polymer with naturally isolated polymeric fraction can also result in an improvement in the thermal stability of the resultant films. Previous reports suggested that

Table 4 Polymer inherent compositional attributes that affect the crystallinity of the films

Common Polymers used in edible films and coating materials	Factors that affect crystallinity	References
Sodium alginate	β -(1–4)-D-mannuronic (M), and α -L-gluronic (G) acids M/G ratio and average molecular weight	[80]
Pectin	Polygalacturonic acid (esterified with methyl groups and the free acid groups) linked with many sugars. Degree of methylation and source of carboxylic acid residues. Pectin is categorized into high-methylation (with more than 50% of carboxyl groups) and low-methylation (with less than 50% of methyl-esterified groups) according to the degree of methylation.	[80]
Gelatin	Hydroxyproline and proline amino acids content. The crystalline state of gelatin is characterized by the presence of triple helices and clusters of helical structures derived from denatured collagen. Conversely, the amorphous state is characterized by colloidal chains that arrange into polyproline helices, referred to as simple helices. This phenomenon arises due to the substantial proportion of proline residues within the gelatin chains, which contribute to the formation of turns in protein chains. The origin of the gelatin source and the process of ageing have discernible effects on its secondary structure and its ability to dissolve in water.	[81]
Hemicellulose	Amorphous, not crystalline as cellulose	[82]
Carboxy methyl cellulose	Large hexagonal-like platelet crystals	[83]
Chitosan	The configuration of the chitosan's crystal lattice is influenced by both its deacetylation process and the polymorphic form of its chitin constituent (including α , β , and γ) since these attributes exert a noticeable effect on the size of the crystal.	[84]
Starches	The degree of crystalline structure observed within starch-derived films ranges from 15–45%, as determined by the proportions of amylose (20–25%) and amylopectin (75–80%) present. The formation of crystalline regions is attributed to the presence of compact amylopectin chains with limited branching, while the generation of amorphous regions is attributed to the branching patterns of both amylose and amylopectin molecules.	[85]
Collagen	The molecular conformation is characterized by a triple helical arrangement, wherein the constituent strands exhibit a recurrent sequence denoted as Xaa-Yaa-Gly. Within this context, the residues L-Proline (Pro) and 4(R)-hydroxyl-L-proline (4(R)Hyp) are commonly found within the Xaa and Yaa positions of said sequence repetition.	[86]
Casein	Minimal secondary or tertiary conformation, disulfide linkages, α -helices, and β -sheets formed by the proline-rich peptides within the casein molecular structure.	[87]

chitosan-corn cob biocomposite films showed improvement in thermal stability by 15 °C [99].

Similarly, the combination of chitosan with thermoplastic polymers, like poly(butylene succinate), poly(-butylene terephthalate adipate), and poly(butylene succinate adipate) is an alternate approach to increase the heat resistance of the films [100]. Another example of improvement in thermal stability was observed when chitin– bentonite blend film was made [101]. The collagen-based film usually offers good barrier properties against oxygen and water vapor however offers a rough surface and poor thermal resistance. Acid hydrolysis of collagen generally allows destabilization of its triple helix, resulting in the formation of soluble gelatin [102]. In gelatin-based films, triple helix content, molecular weight and amino acid composition are the critical factors that impact the thermal stability of the resultant films [102]. Agar-based films are highly brittle and possess poor thermal properties [103]. Sodium alginate is often used as a common ingredient among several edible films based on recent research. The composition, sequence, and proportion of alginate monomers M immediately impact the properties of alginate-based films. Domination of G-monomers results in strong films whereas dominance of M-monomers leads to more elastic films. This is mainly dependent on its

interaction with metal cations, such as calcium ions as such interaction between monomers and metal ions resulted in the formation of a stable and ordered 3-D “egg box” model grid. Due to the selectivity of the monomers, especially G monomer, it is important to add a suitable crosslinker which can help in the formation of a stable complex to improve the thermal stability of the film [104].

Cellulose-based films are commonly used in the form of edible films. Cellulose generally shows degradation at the temperature of 350 °C [105]. On the other side cellulose nanocrystals or nanocellulose are highly crystalline materials with improved thermal properties [106]. The incorporation of nanocellulose having a low thermal expansion coefficient can improve the thermal stability of the films [106]. Similarly, highly thermal-resistant proteins such as zein can also improve the thermal stability of the edible films [107]. Poly(lactic acid) is also known for its good thermal properties which are dependent on D and L ratio (two mesoforms). Its barrier and mechanical strength properties are comparable to polystyrene. Thus, its suitable blend can improve the thermal resistance of the other polymer films [108]. Several polyhydroxyalkanoates have been reported for their comparable thermal properties like PE, PS, and PP [108]. The thermal resistance of the biopolymer-based films

can be improved with the incorporation of graphene, clays, cellulose nanocrystals (nanofillers), and metal oxides [108]. The degradation temperature of films can be extended by using such components as these substances are effective in reducing biocomposite thermal degradation [109]. In addition to the chemical nature, thermal and irradiation treatments can also improve the thermal resistance of the films. Coupling thermal treatment with irradiation can also be utilized to fabricate the films with better thermal stability [110]. Exposure of films to radiation can also result in films with denser networks via rearrangement of chain improvement increasing the thermal stability of the films. For an instance thermal stability of composite gelatin-nutshell fiber was increased after a 40 kGy electron beam irradiation dose [111]. Previous research also demonstrated the use of ultrasonication in developing transparent cellulose film from ginger nanofiber with improved thermal stability [112].

Nanoreinforcements in Edible Films and Their Effect on Thermal Stability

Transformation of the macroscale materials to nanoscale (1–100 nm) allows significant manipulation of the physical and chemical attributes of the material. Food nanoscience is one of the most advanced areas that permits nano reinforcement of biobased materials to offer material with better properties [113]. Due to the suitable size, the nano reinforcements offer a relatively larger surface area per mass of additive than the micro-reinforcements, which allows better interaction with the polymer matrix [114]. Thus, it could be expected that the resultant materials could present improved thermal properties. This nano-fortification of biopolymers can be succeeded with minimal filling volume whereas macro fortification traditionally requires higher filler volume to attain a similar effect. This approach results in a decline in the weight of the packaging material with improved thermal and other properties in the similar polymer matrix. These nanofillers for edible films are classified as organic (clay minerals, polysaccharides) and inorganic materials (metal or metal oxides) [115]. Due to their thermal stability, more stress is retained on inorganic fillers mainly iron oxide (Fe₃O₄), silver (Ag), gold (Au), titanium oxide (TiO₂), zinc oxide (ZnO), copper oxide (CuO), cerium dioxide hydroxides, aluminium oxides, calcium carbonate and carbon-based materials [116, 117].

Nanoclays (e.g., halloysite, montmorillonite, bentonite, kaolinite, sepiolite, and Laponite[®]) have been used to reinforce the polymers in food packaging materials [118]. The addition of these nanomaterials in the edible films can improve their thermal resistance. Different types of thermodynamically possible composites can be achieved when a

polymer and the clay are amalgamated (Tactoids, Intercalated, Exfoliated). This arrangement impacts the thermal stability of the whole formulation [119]. Films synthesized from a single material often offer poor thermal stability [120]. Nanocellulose, nanostarch, and nanochitosan-based nano-reinforcements of edible films have been reported to improve the thermal resistance of biopolymers. Cellulose nanocrystals from bacterial cellulose produced by *Gluconacetobacter xylinus* were loaded into a gelatin matrix to prepare edible nanocomposites with improved thermal properties [121]. Sessini et al. [122] extracted starch nanocrystals from waxy cornstarch granules through acid hydrolysis and used these particles to increase the mechanical attributes and thermal stability of glycerol-plasticized potato starch edible films [122]. Starch nanocrystals have been used in edible films to improve crystallinity and thermal profile [123]. These starch nanocrystals have been recently synthesized to improve the thermal resistance of starch films [124]. Chitosan nanoparticles have been used to improve the thermal stability of pectin-based nanocomposite edible films and starch/guar gum-based coating materials [125–127].

Among inorganic materials, nanoscale hydroxyapatite (an inorganic component of bones and teeth) has been reported to improve the thermal properties of bovine skin-derived type A gelatin films [128]. Similarly, magnesium hydroxide nanoplates loaded in a pectin matrix improved thermal properties [129].

Effect of Crosslinkers on Thermal Stability of Edible Films

The cross-linking approach is one of the conventional and reliable approaches to chemically modify a polymer, resulting in a material with improved thermal resistance. This approach makes the films more resistant to heat and at the same time offers a superior level of dimensional stability, mechanical strength, and chemical and solvent resistance. Crosslinking improves the polymer's thermal stability by reducing the molecular rotation and vibration that occurs during thermal excitation [130]. The thermal properties of the films are significantly impacted by the extent of crosslinking, the regularity of the resultant material, and the percentage of crystallinity. The addition of natural (tannic, gallic, caffeic, ferulic) acids, or synthetic crosslinkers (formaldehyde and glutaraldehyde, carbodiimides, polyepoxy compounds, acylazide etc.) can improve the thermal stability of the edible films [91, 131, 132]. Additionally, some other natural agents such as genipin, flavonoids (catechin, flavone, or quercetin) carboxylic acids (malic acid,

citric acid, and succinic acid) and xylose also showed cross-linking effects on the films [133–135][132].

The addition of crosslinkers can produce larger molecular aggregates resulting in an enhanced film-forming solution with high viscosity characteristics. These crosslinkers increase the covalent bonding, to establish stronger intermolecular covalent bonds, to attain closer molecular packing and reduced polymer mobility [136]. These crosslinkers can efficiently improve intramolecular cross-linking (in polymer) or intermolecular cross-linking (between polymers). Carbodiimide is also utilized as a potential crosslinkers in the food packaging industry [91]. The addition of gallic acid improved the thermal stability of gelatin and casein-based composite films [133].

The incorporation of pectin /sodium alginate via cross-linking with citric acid and tartaric acid slightly improved the thermal stability of the composite films [137]. The inclusion of citric acid in carboxymethyl chitosan/poly(vinyl alcohol) improved the thermal stability of the films [138]. Xylose has also improved the thermal stability of grasshopper protein/soy protein isolate/cinnamaldehyde films [132]. The thermal stability of the casein films was improved by crosslinking with tannic acid [139]. Crosslinking can also be achieved by ionic gelation (metallic ions), electrostatic interactions (opposite charge to form PEC), and a

self-assembly process. However, the amount and type of crosslinker and type of polymer matrix determine the extent of the crosslinking reaction. Figure 3 shows the effect of incorporating crosslinkers in the formation of edible films.

Final Remarks

Due to renewable, biodegradable, and relatively high safety profile, natural polymeric films are considered potential replacements for conventional plastic-based packaging. However, these biobased films failed to offer high mechanical and thermal stability equivalent to synthetic food packaging materials. The low thermal resistance of the biopolymeric films and their unsatisfactory thermal stability profile always hinder their reachability to the market. Advance understanding of thermal analytical tools and approaches to cater more information from thermograms of biopolymeric films could help in determining their thermal stability efficiently. Additionally, the thermal degradation profile of neat biopolymeric films offers useful information about native polymer thermal stability that helps in designing the composite formulation with relatively high thermal resistant films. The design and development of stable heat-sealable biopolymeric films need more emphasis on their

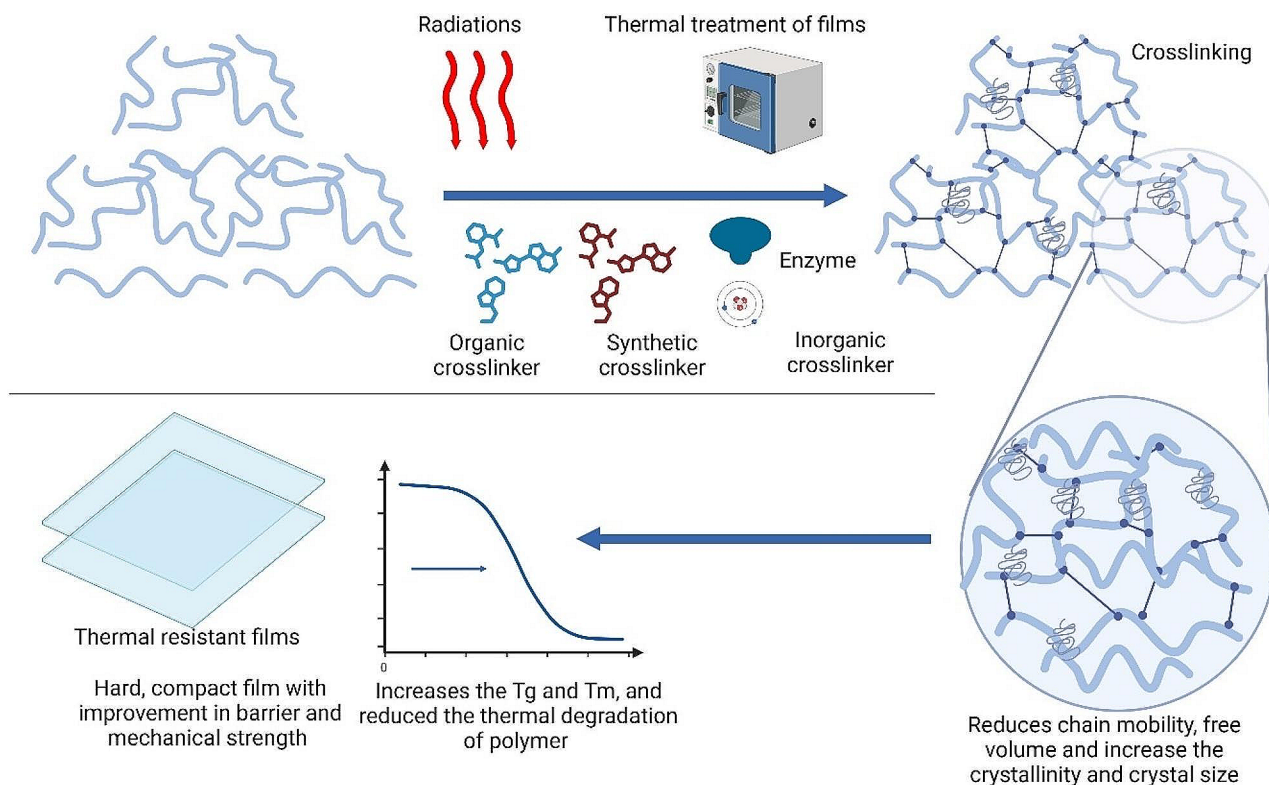


Fig. 3 Effect of the crosslinkers on the thermal stability of the films

fluctuating crystallinity, morphology, thickness, and other parameters under unfavourable temperature conditions. Composition, especially the incorporation of additives in the case of active packaging films plays a vital role in regulating the thermal profile of the biopolymeric films. With the growing interest in sustainable and eco-friendly packaging solutions, the insights presented in this review can have a significant impact on the development of future food packaging technologies that prioritize both functionality and environmental considerations.

Acknowledgements The Authors are thankful to the Natural and Medical Sciences Research Center, University of Nizwa, Oman, for providing literature collection facilities, and the BC Food and Beverage Innovation Centre, University of British Columbia, Vancouver, Canada for providing leadership to the international effort.

Author Contributions Conceptualization. Yasir Abbas Shah, Saurabh Bhatia and Ahmed Al-Harrasi; formal analysis, Fatih Oz, Mujahid Hassan Khan, Swarup Roy; writing—original draft preparation, Yasir Abbas Shah, Saurabh Bhatia and Ahmed Al-Harrasi; writing—review and editing, Tuba Esatbeyoglu, and Anubhav Pratap-Singh. All authors reviewed the manuscript.

Funding The study was supported by TRC grant number BFP/RGP/HSS/22/007.

Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing Interests The authors declare no competing interests.

Informed Consent Not applicable.

References

- Gupta RK, Guha P, Srivastav PP (2022) Natural polymers in bio-degradable/edible film: a review on environmental concerns, cold plasma technology and nanotechnology application on food packaging-A recent trends. *Food Chem Adv* 1:100135
- Bhatia S, Al-Harrasi A, Shah YA, Altoubi HWK, Kotta S, Sharma P, Anwer MK, Kaithavalappil DS, Koca E, Aydemir LY (2023) Fabrication, characterization, and Antioxidant Potential of Sodium Alginate/Acacia Gum Hydrogel-based films loaded with Cinnamon essential oil. *Gels* 9(4):337
- Singh S, Gaikwad KK, Lee M, Lee YS (2018) Temperature-regulating materials for advanced food packaging applications: a review. *J Food Meas Charact* 12:588–601
- Chalco-Sandoval W, Fabra MJ, López-Rubio A, Lagaron JM (2015) Development of polystyrene-based films with temperature buffering capacity for smart food packaging. *J Food Eng* 164:55–62
- Patti A, Acierno D (2020) Thermal conductivity of polypropylene-based materials. *Polypropylene—Polymerization And Characterization Of Mechanical And Thermal Properties*
- Ganeson K, Razifah M, Mubarak A, Kam A, Vigneswari S, Ramakrishna S (2022) Improved functionality of cinnamon oil emulsion-based gelatin films as potential edible packaging film for wax apple. *Food Bioscience* 47:101638
- Prime RB, Bair HE, Vyazovkin S, Gallagher PK, Riga A (2009) Thermogravimetric analysis (TGA). *Thermal analysis of polymers: Fundamentals and applications*, 241–317
- Bhatia S, Shah YA, Al-Harrasi A, Jawad M, Koca E, Aydemir LY (2024) Novel applications of black pepper essential oil as an antioxidant agent in sodium caseinate and chitosan based active edible films. *Int J Biol Macromol* 254:128045
- Ramgobin A, Fontaine G, Bourbigot S (2019) Thermal degradation and fire behavior of high performance polymers. *Polym Rev* 59(1):55–123
- Sedaghat E, Rostami AA, Ghaemy M, Rostami A (2019) Characterization, thermal degradation kinetics, and morphological properties of a graphene oxide/poly (vinyl alcohol)/starch nanocomposite. *J Therm Anal Calorim* 136:759–769
- Teixeira-Costa BE, Ferreira WH, Goycoolea FM, Murray BS, Andrade CT (2023) Improved antioxidant and mechanical properties of food packaging films based on chitosan/deep eutectic solvent, containing açai-filled microcapsules. *Molecules* 28(3):1507
- Mondal K, Bhattacharjee SK, Mudenur C, Ghosh T, Goud VV, Katiyar V (2022) Development of antioxidant-rich edible active films and coatings incorporated with de-oiled ethanolic green algae extract: a candidate for prolonging the shelf life of fresh produce. *RSC Adv* 12(21):13295–13313
- Li H, Liu C, Sun J, Lv S (2022) Bioactive Edible Sodium Alginate Films Incorporated with tannic acid as Antimicrobial and Antioxidative Food Packaging. *Foods* 11(19):3044
- Aziz MSA, Salama HE, Sabaa MW (2018) Biobased alginate/castor oil edible films for active food packaging. *Lwt* 96:455–460
- Marangoni Júnior L, Rodrigues PR, da Silva RG, Vieira RP, Alves RMV (2021) Sustainable packaging films composed of sodium alginate and hydrolyzed collagen: preparation and characterization. *Food Bioprocess Technol* 14:2336–2346
- Zhou F, Wang D, Zhang J, Li J, Lai D, Lin S, Hu J (2022) Preparation and characterization of biodegradable κ-carrageenan based anti-bacterial film functionalized with Wells-Dawson polyoxometalate. *Foods* 11(4):586
- Martins JT, Cerqueira MA, Bourbon AI, Pinheiro AC, Souza BW, Vicente AA (2012) Synergistic effects between κ-carrageenan and Locust bean gum on physicochemical properties of edible films made thereof. *Food Hydrocolloids* 29(2):280–289
- Wang K, Wang W, Ye R, Xiao J, Liu Y, Ding J, Zhang S, Liu A (2017) Mechanical and barrier properties of maize starch–gelatin composite films: effects of amylose content. *J Sci Food Agric* 97(11):3613–3622
- Nunes JC, Melo PTS, Lorevice MV, Aouada FA, de Moura MR (2021) Effect of green tea extract on gelatin-based films incorporated with lemon essential oil. *J Food Sci Technol* 58(1):1–8
- Šešlija S, Nešić A, Ružić J, Krušić MK, Veličković S, Avolio R, Santagata G, Malinconico M (2018) Edible blend films of pectin and poly (ethylene glycol): Preparation and physico-chemical evaluation. *Food Hydrocolloids* 77:494–501
- Nesic A, Meseldzija S, Cabrera-Barjas G, Onjia A (2022) Novel biocomposite films based on high methoxyl pectin reinforced with zeolite Y for food packaging applications. *Foods* 11(3):360
- Seiwert K, Kamdem D-P, Kocabaş DS, Ustunol Z (2021) Development and characterization of whey protein isolate and xylan composite films with and without enzymatic crosslinking. *Food Hydrocolloids* 120:106847
- Gomaa M, Al-Badaani AA, Hifney AF, Adam MS (2022) Utilization of cellulose and ulvan from the green seaweed *Ulva lactuca* in the development of composite edible films with natural antioxidant properties. *J Appl Phycol* 34(5):2615–2626
- Leyva-Porras C, Cruz-Alcantar P, Espinosa-Solis V, Martínez-Guerra E, Piñón-Balderrama CI, Martínez C, I., Saavedra-Leos

- MZ (2019) Application of differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC) in food and drug industries. *Polymers* 12(1):5
25. Rahman MS, Al-Marhubi IM, Al-Mahrouqi A (2007) Measurement of glass transition temperature by mechanical (DMTA), thermal (DSC and MDSC), water diffusion and density methods: a comparison study. *Chem Phys Lett* 440(4–6):372–377
 26. Kadzińska J, Bryś J, Ostrowska-Ligeża E, Estéve M, Janowicz M (2020) Influence of vegetable oils addition on the selected physical properties of apple–sodium alginate edible films. *Polym Bull* 77:883–900
 27. Hernández-López M, Correa-Pacheco ZN, Bautista-Baños S, Zavaleta-Avejar L, Benítez-Jiménez JJ, Sabino-Gutiérrez MA, Ortega-Gudiño P (2019) Bio-based composite fibers from pine essential oil and PLA/PBAT Polymer blend. Morphological, physicochemical, thermal and mechanical characterization. *Mater Chem Phys* 234:345–353
 28. Gharanjig H, Gharanjig K, Hosseinezhad M, Jafari SM (2020) Differential scanning calorimetry (DSC) of nanoencapsulated food ingredients. Characterization of nanoencapsulated food ingredients. Elsevier, pp 295–346
 29. Pijpers M, Mathot V (2008) Optimization of instrument response and resolution of standard-and high-speed power compensation DSC: benefits for the study of crystallization, melting and thermal fractionation. *J Therm Anal Calorim* 93:319–327
 30. Harnkarnsujarit N (2017) Glass-transition and non-equilibrium states of edible films and barriers. Non-equilibrium states and glass transitions in foods. Elsevier, pp 349–377
 31. Tulamandi S, Rangarajan V, Rizvi SS, Singhal RS, Chattopadhyay SK, Saha NC (2016) A biodegradable and edible packaging film based on papaya puree, gelatin, and defatted soy protein. *Food Packaging Shelf Life* 10:60–71
 32. Mutlur S (2004) Thermal analysis of composites using DSC. *Adv Top Charact Compos*, 11–33
 33. Chakraborty I, Rongpipi S, Govindaraju I, Mal SS, Gomez EW, Gomez ED, Kalita RD, Nath Y, Mazumder N (2022) An insight into microscopy and analytical techniques for morphological, structural, chemical, and thermal characterization of cellulose. *Microsc Res Tech* 85(5):1990–2015
 34. Iijima M, Nakamura K, Hatakeyama T, Hatakeyama H (2000) Phase transition of pectin with sorbed water. *Carbohydr Polym* 41(1):101–106
 35. Einhorn-Stoll U, Kunzek H, Dongowski G (2007) Thermal analysis of chemically and mechanically modified pectins. *Food Hydrocolloids* 21(7):1101–1112
 36. Nisar T, Wang Z-C, Alim A, Iqbal M, Yang X, Sun L, Guo Y (2019) Citrus pectin films enriched with thinned young apple polyphenols for potential use as bio-based active packaging. *CyTA-Journal Food* 17(1):695–705
 37. Jahromi M, Niakousari M, Golmakani MT, Mohammadifar MA (2020) Physicochemical and structural characterization of sodium caseinate based film-forming solutions and edible films as affected by high methoxyl pectin. *Int J Biol Macromol* 165:1949–1959
 38. Kaya M, Khadem S, Cakmak YS, Mujtaba M, Ilk S, Akyuz L, Salaberria AM, Labidi J, Abdulqadir AH, Deligöz E (2018) Antioxidative and antimicrobial edible chitosan films blended with stem, leaf and seed extracts of Pistacia terebinthus for active food packaging. *RSC Adv* 8(8):3941–3950
 39. Kaya M, Ravikumar P, Ilk S, Mujtaba M, Akyuz L, Labidi J, Salaberria AM, Cakmak YS, Erkul SK (2018) Production and characterization of Chitosan based edible films from Berberis Crataegina's fruit extract and seed oil. *Innovative Food Sci Emerg Technol* 45:287–297
 40. Staroszczyk H, Pieliowska J, Sztuka K, Stangret J, Kołodziejska I (2012) Molecular and structural characteristics of cod gelatin films modified with EDC and TGase. *Food Chem* 130(2):335–343
 41. Arfat YA, Ejaz M, Jacob H, Ahmed J (2017) Deciphering the potential of guar gum/Ag-Cu nanocomposite films as an active food packaging material. *Carbohydr Polym* 157:65–71
 42. Mosleh Y, de Zeeuw W, Nijemeisland M, Bijleveld JC, van Duin P, Poullis JA (2021) The structure–property correlations in dry gelatin adhesive films. *Adv Eng Mater* 23(1):2000716
 43. Silva GGD, d., Sobral PJA, Carvalho RAd, Bergo PVA, Mendieta-Taboada O, Habitante A (2008) Biodegradable films based on blends of gelatin and poly (vinyl alcohol): effect of PVA type or concentration on some physical properties of films. *J Polym Environ* 16:276–285
 44. Kilinc D, Ocak B, Özdestand-Ocak Ö (2021) Preparation, characterization and antioxidant properties of gelatin films incorporated with Origanum onites L. essential oil. *J Food Meas Charact* 15:795–806
 45. Scartazzini L, Tosati J, Cortez D, Rossi M, Flôres S, Hubinger M, Di Luccio M, Monteiro A (2019) Gelatin edible coatings with mint essential oil (*Mentha arvensis*): Film characterization and antifungal properties. *J Food Sci Technol* 56:4045–4056
 46. Hosseini SF, Rezaei M, Zandi M, Farahmandghavi F (2015) Bio-based composite edible films containing Origanum vulgare L. essential oil. *Ind Crops Prod* 67:403–413
 47. Qin Y, Li W, Liu D, Yuan M, Li L (2017) Development of active packaging film made from poly (lactic acid) incorporated essential oil. *Prog Org Coat* 103:76–82
 48. Lu W, Cui R, Zhu B, Qin Y, Cheng G, Li L, Yuan M (2021) Influence of clove essential oil immobilized in mesoporous silica nanoparticles on the functional properties of poly (lactic acid) biocomposite food packaging film. *J Mater Res Technol* 11:1152–1161
 49. Dong M, Tian L, Li J, Jia J, Dong Y, Tu Y, Liu X, Tan C, Duan X (2022) Improving physicochemical properties of edible wheat gluten protein films with proteins, polysaccharides and organic acid. *Lwt* 154:112868
 50. Sayanjali S, Ghanbarzadeh B, Ghiassifar S (2011) Evaluation of antimicrobial and physical properties of edible film based on carboxymethyl cellulose containing potassium sorbate on some mycotoxigenic aspergillus species in fresh pistachios. *LWT-Food Sci Technol* 44(4):1133–1138
 51. Nuvoli L, Conte P, Fadda C, Ruiz JAR, García JM, Baldino S, Mannu A (2021) Structural, thermal, and mechanical properties of gelatin-based films integrated with tara gum. *Polymer* 214:123244
 52. Menard KP, Menard N (2020) Dynamic mechanical analysis. CRC
 53. Artiaga R, García-Diez A (2005) Fundamentals of DMA.
 54. Dunson D (2017) Characterization of polymers using dynamic mechanical analysis (DMA). *EAG Appl Note*
 55. Jones DS (1999) Dynamic mechanical analysis of polymeric systems of pharmaceutical and biomedical significance. *Int J Pharm* 179(2):167–178
 56. James J (2017) Thermomechanical analysis and its applications. Thermal and rheological measurement techniques for nanomaterials characterization. Elsevier, pp 159–171
 57. Saba N, Jawaid M (2018) A review on thermomechanical properties of polymers and fibers reinforced polymer composites. *J Ind Eng Chem* 67:1–11
 58. Wang H, Ding F, Ma L, Zhang Y (2021) Edible films from chitosan-gelatin: physical properties and food packaging application. *Food Bioscience* 40:100871
 59. Naseri HR, Beigmohammadi F, Mohammadi R, Sadeghi E (2020) Production and characterization of edible film based on gelatin–chitosan containing Ferulago Angulate essential oil and its

- application in the prolongation of the shelf life of Turkey meat. *J Food Process Preserv* 44(8):e14558
60. Benbettaieb N, Karbowski T, Debeaufort F (2019) Bioactive edible films for food applications: influence of the bioactive compounds on film structure and properties. *Crit Rev Food Sci Nutr* 59(7):1137–1153
 61. Sandhu KS, Sharma L, Kaur M, Kaur R (2020) Physical, structural and thermal properties of composite edible films prepared from pearl millet starch and carrageenan gum: process optimization using response surface methodology. *Int J Biol Macromol* 143:704–713
 62. Zhou Y, Wu X, Chen J, He J (2021) Effects of Cinnamon essential oil on the physical, mechanical, structural and thermal properties of cassava starch-based edible films. *Int J Biol Macromol* 184:574–583
 63. Rajeshwar MS, Anokhi C (2021) Development and application of Edible Film with bioactive compound. *Int J Food Sci Nutr Dietetics (IJFS)* 10(2):524–531
 64. Matta Fakhouri F, Nogueira GF, de Oliveira RA, Velasco JI (2019) Bioactive edible films based on arrowroot starch incorporated with cranberry powder: microstructure, thermal properties, ascorbic acid content and sensory analysis. *Polymers* 11(10):1650
 65. Azeredo HM, Morrugares-Carmona R, Wellner N, Cross K, Bajka B, Waldron KW (2016) Development of pectin films with pomegranate juice and citric acid. *Food Chem* 198:101–106
 66. Ivanič F, Jochec-Mošková D, Janigová I, Chodák I (2017) Physical properties of starch plasticized by a mixture of plasticizers. *Eur Polymer J* 93:843–849
 67. Kumar N, Pratibha T, Petkoska A, Khojah E, Sami R, Al-Mushhin AA (2021) Chitosan edible films enhanced with pomegranate peel extract: study on physical, biological, thermal, and barrier properties. *Materials* 14(12):3305
 68. Meerasri J, Sothornvit R (2020) Characterization of bioactive film from pectin incorporated with gamma-aminobutyric acid. *Int J Biol Macromol* 147:1285–1293
 69. Zhelyazkov S, Zsivanovits G, Stamenova E, Marudova M (2022) Physical and barrier properties of clove essential oil loaded potato starch edible films. *Biointerface Res Appl Chem* 12:4603–4612
 70. Bhatia S, Al-Harrasi A, Shah YA, Jawad M, Al-Azri MS, Ullah S, Anwer MK, Aldawsari MF, Koca E, Aydemir LY (2023) Physicochemical characterization and antioxidant properties of Chitosan and Sodium Alginate Based Films Incorporated with Ficus Extract. *Polymers* 15(5):1215
 71. Jridi M, Boughriba S, Abdelhedi O, Nciri H, Nasri R, Kchaou H, Kaya M, Sebai H, Zouari N, Nasri M (2019) Investigation of physicochemical and antioxidant properties of gelatin edible film mixed with blood orange (*Citrus sinensis*) peel extract. *Food Packaging Shelf Life* 21:100342
 72. Matta E, Tavera-Quiroz MJ, Bertola N (2019) Active edible films of methylcellulose with extracts of green apple (Granny Smith) skin. *Int J Biol Macromol* 124:1292–1298
 73. He B, Wang W, Song Y, Ou Y, Zhu J (2020) Structural and physical properties of carboxymethyl cellulose/gelatin films functionalized with antioxidant of bamboo leaves. *Int J Biol Macromol* 164:1649–1656
 74. Chakravartula SSN, Lourenço RV, Balestra F, Bittante AMQB, do Amaral Sobral PJ, Dalla Rosa M (2020) Influence of pitanga (*Eugenia uniflora* L.) leaf extract and/or natamycin on properties of cassava starch/chitosan active films. *Food Packaging Shelf Life* 24:100498
 75. Germann LS, Carlino E, Taurino A, Magdysyuk OV, Voinovich D, Dinnebieer RE, Bučar DK, Hasa D (2023) Modulating thermal properties of polymers through crystal engineering. *Angew Chem Int Ed* 62(19):e202212688
 76. Bunaciu AA, UdrișTioiu EG, Aboul-Enein HY (2015) X-ray diffraction: instrumentation and applications. *Crit Rev Anal Chem* 45(4):289–299
 77. Tafa KD, Satheesh N, Abera W (2023) Mechanical properties of tef starch based edible films: development and process optimization. *Heliyon*, 9(2)
 78. Bai L-f, Li X-x, Li H, Sun G-a, Liu D, Peng M, Zhu Z-c, Huang C-q, Gong F-y, Li S-c (2023) A review of small angle scattering, neutron reflection, and neutron diffraction techniques for microstructural characterization of polymer-bonded explosives. *Energetic Mater Front* 4(3):140–157
 79. Gilbert EP (2019) Small-angle X-Ray and neutron scattering in food colloids. *Curr Opin Colloid Interface Sci* 42:55–72
 80. Jiao W, Chen W, Mei Y, Yun Y, Wang B, Zhong Q, Chen H, Chen W (2019) Effects of molecular weight and guluronic acid/mannuronic acid ratio on the rheological behavior and stabilizing property of sodium alginate. *Molecules* 24(23):4374
 81. Duconseille A, Wien F, Audonnet F, Traore A, Refregiers M, Astruc T, Santé-Lhoutellier V (2017) The effect of origin of the gelatine and ageing on the secondary structure and water dissolution. *Food Hydrocolloids* 66:378–388
 82. Brunner G (2014) Processing of biomass with hydrothermal and supercritical water. *Supercritical Fluid Science and Technology*, vol 5. Elsevier, pp 395–509
 83. Yu M, Wang Z, Tian M, Lu C, Li S, Du H (2016) Purinyl N3-Directed Palladium-Catalyzed C–H alkoxylation of N 9-Arylpurines: a late-stage strategy to synthesize N 9-(ortho-Alkoxy) arylpurines. *J Org Chem* 81(8):3435–3442
 84. Jampafuang Y, Tongta A, Waiprib Y (2019) Impact of crystalline structural differences between α - and β -chitosan on their nanoparticle formation via ionic gelation and superoxide radical scavenging activities. *Polymers*, 11(12), 2010
 85. Singh GP, Bangar SP, Yang T, Trif M, Kumar V, Kumar D (2022) Effect on the properties of edible starch-based films by the incorporation of additives: a review. *Polymers* 14(10):1987
 86. Schumacher MA, Mizuno K, Bachinger HP (2006) The crystal structure of a collagen-like polypeptide with 3 (S)-hydroxyproline residues in the xaa position forms a standard 7/2 collagen triple helix. *J Biol Chem* 281(37):27566–27574
 87. Khan MR, Volpe S, Valentino M, Miele NA, Cavella S, Torrieri E (2021) Active casein coatings and films for perishable foods: structural properties and shelf-life extension. *Coatings* 11(8):899
 88. Suyatna NE, Tighzert L, Copinet A, Coma V (2005) Effects of hydrophilic plasticizers on mechanical, thermal, and surface properties of chitosan films. *J Agric Food Chem* 53(10):3950–3957
 89. Basiak E, Lenart A, Debeaufort F (2017) Effect of starch type on the physico-chemical properties of edible films. *Int J Biol Macromol* 98:348–356
 90. Jeevahan JJ, Chandrasekaran M, Venkatesan S, Sriram V, Joseph GB, Mageshwaran G, Durairaj R (2020) Scaling up difficulties and commercial aspects of edible films for food packaging: a review. *Trends Food Sci Technol* 100:210–222
 91. Garavand F, Rouhi M, Razavi SH, Cacciotti I, Mohammadi R (2017) Improving the integrity of natural biopolymer films used in food packaging by crosslinking approach: a review. *Int J Biol Macromol* 104:687–707
 92. Xu X, Chen J, Zhou J, Li B (2018) Thermal conductivity of polymers and their nanocomposites. *Adv Mater* 30(17):1705544
 93. Xue Y, Lofland S, Hu X (2019) Thermal conductivity of protein-based materials: a review. *Polymers* 11(3):456
 94. Díaz-Galindo EP, Nesic A, Cabrera-Barjas G, Mardones C, Von Baer D, Bautista-Baños S, Garcia D, O (2020) Physical-chemical evaluation of active food packaging material based on thermoplastic starch loaded with grape cane extract. *Molecules* 25(6):1306

95. Galindez A, Daza LD, Homez-Jara A, Eim VS, Váquiro HA (2019) Characterization of ulluco starch and its potential for use in edible films prepared at low drying temperature. *Carbohydr Polym* 215:143–150
96. Zhao S, Malfait WJ, Guerrero-Alburquerque N, Koebel MM, Nyström G (2018) Biopolymer aerogels and foams: Chemistry, properties, and applications. *Angew Chem Int Ed* 57(26):7580–7608
97. Mitra T, Sailakshmi G, Gnanamani A, Raja STK, Thiruselvi T, Gowri VM, Selvaraj NV, Ramesh G, Mandal A (2011) Preparation and characterization of a thermostable and biodegradable biopolymers using natural cross-linker. *Int J Biol Macromol* 48(2):276–285
98. Barbosa HF, Francisco DS, Ferreira AP, Cavalheiro ÉT (2019) A new look towards the thermal decomposition of chitins and chitosans with different degrees of deacetylation by coupled TG-FTIR. *Carbohydr Polym* 225:115232
99. Chan H, Nyam K, Yusof Y, Pui L (2020) INVESTIGATION OF PROPERTIES OF POLYSACCHARIDE-BASED EDIBLE FILM INCORPORATED WITH FUNCTIONAL MELASTOMA MALABATHRICUM EXTRACT. *Carpathian J Food Sci Technol*, 12(1)
100. van den Broek LA, Knoop RJ, Kappen FH, Boeriu CG (2015) Chitosan films and blends for packaging material. *Carbohydr Polym* 116:237–242
101. Saravanan D, Hemalatha R, Sudha P (2011) Synthesis and characterization of cross linked chitin/bentonite polymer blend and adsorption studies of Cu (II) and Cr (VI) on chitin. *Der Pharma Chem* 3(6):406–424
102. Ross-Murphy SB (1992) Structure and rheology of gelatin gels: recent progress. *Polymer* 33(12):2622–2627
103. Deiber JA, Ottone ML, Piaggio MV, Peirotti MB (2009) Characterization of cross-linked polyampholytic gelatin hydrogels through the rubber elasticity and thermodynamic swelling theories. *Polymer* 50(25):6065–6075
104. Ferreira AR, Alves VD, Coelho IM (2016) Polysaccharide-based membranes in food packaging applications. *Membranes* 6(2):22
105. Poletto M, Zattera AJ, Forte MM, Santana RM (2012) Thermal decomposition of wood: influence of wood components and cellulose crystallite size. *Bioresour Technol* 109:148–153
106. Benito-González I, Jaén-Cano CM, López-Rubio A, Martínez-Abad A, Martínez-Sanz M (2020) Valorisation of vine shoots for the development of cellulose-based biocomposite films with improved performance and bioactivity. *Int J Biol Macromol* 165:1540–1551
107. Fabra MJ, Lopez-Rubio A, Lagaron JM (2013) High barrier polyhydroxycanoate food packaging film by means of nanostructured electrospun interlayers of zein. *Food Hydrocolloids* 32(1):106–114
108. Barra A, Santos JD, Silva MR, Nunes C, Ruiz-Hitzky E, Gonçalves I, Yildirim S, Ferreira P, Marques PA (2020) Graphene derivatives in biopolymer-based composites for food packaging applications. *Nanomaterials*, 10(10), 2077
109. Li F, Yu H-Y, Wang Y-Y, Zhou Y, Zhang H, Yao J-M, Abdalkarim SYH, Tam KC (2019) Natural biodegradable poly (3-hydroxybutyrate-co-3-hydroxyvalerate) nanocomposites with multifunctional cellulose nanocrystals/graphene oxide hybrids for high-performance food packaging. *J Agric Food Chem* 67(39):10954–10967
110. Sabato S, Ouattara B, Yu H, D'aprano G, Le Tien C, Mateescu M, Lacroix M (2001) Mechanical and barrier properties of cross-linked soy and whey protein based films. *J Agric Food Chem* 49(3):1397–1403
111. Inamura PY, Kraide FH, Drumond WS, de Lima NB, Moura EA, del Mastro NL (2013) Ionizing radiation influence on the morphological and thermal characteristics of a biocomposite prepared with gelatin and Brazil nut wastes as fiber source. *Radiat Phys Chem* 84:66–69
112. Mahardika M, Abrial H, Kasim A, Arief S, Hafizulhaq F, Asrofi M (2019) Properties of cellulose nanofiber/bengkoang starch bionanocomposites: Effect of fiber loading. *Lwt* 116:108554
113. Odetayo T, Tesfay S, Ngobese NZ (2022) Nanotechnology-enhanced edible coating application on climacteric fruits. *Food Sci Nutr* 10(7):2149–2167
114. Njuguna J, Pielichowski K, Desai S (2008) Nanofiller-reinforced polymer nanocomposites. *Polym Adv Technol* 19(8):947–959
115. Njuguna J, Ansari F, Sachse S, Rodriguez VM, Siqueira S, Zhu H (2021) Nanomaterials, nanofillers, and nanocomposites: types and properties. Health and environmental safety of nanomaterials. Elsevier, pp 3–37
116. Bouwmeester H, Brandhoff P, Marvin HJ, Weigel S, Peters RJ (2014) State of the safety assessment and current use of nanomaterials in food and food production. *Trends Food Sci Technol* 40(2):200–210
117. He X, Hwang H-M (2016) Nanotechnology in food science: functionality, applicability, and safety assessment. *J food drug Anal* 24(4):671–681
118. Deshmukh RK, Hakim L, Akhila K, Ramakanth D, Gaikwad KK (2023) Nano clays and its composites for food packaging applications. *Int Nano Lett* 13(2):131–153
119. Nath D, Santhosh R, Pal K, Sarkar P (2022) Nanoclay-based active food packaging systems: a review. *Food Packaging Shelf Life* 31:100803
120. Zhao R, Guan W, Zheng P, Tian F, Zhang Z, Sun Z, Cai L (2022) Development of edible composite film based on chitosan nanoparticles and their application in packaging of fresh red sea bream fillets. *Food Control* 132:108545
121. George J (2012) High performance edible nanocomposite films containing bacterial cellulose nanocrystals. *Carbohydr Polym* 87(3):2031–2037
122. Sessini V, Arrieta MP, Kenny JM, Peponi L (2016) Processing of edible films based on nanoreinforced gelatinized starch. *Polym Degrad Stab* 132:157–168
123. LeCorre D, Bras J, Dufresne A (2012) Influence of native starch's properties on starch nanocrystals thermal properties. *Carbohydr Polym* 87(1):658–666
124. Martins PC, Latorres JM, Martins VG, Machado AV (2022) Effect of starch nanocrystals addition on the physicochemical, thermal, and optical properties of low-density polyethylene (LDPE) films. *Polym Eng Sci* 62(6):1786–1796
125. Ahmed S, Keniry M, Padilla V, Anaya-Barbosa N, Javed MN, Gilkerson R, Gomez K, Ashraf A, Narula AS, Lozano K (2023) Development of pullulan/chitosan/salvianolic acid ternary fibrous membranes and their potential for chemotherapeutic applications. *Int J Biol Macromol*, 126187
126. Dos Santos VS, Lorevice MV, Baccarin GS, da Costa FM, da Silva Fernandes R, Aouada FA, de Moura MR (2023) Combining Chitosan nanoparticles and Garlic essential oil as Additive fillers to produce pectin-based Nanocomposite Edible films. *Polymers* 15(10):2244
127. Lorevice MV, Otoni CG, de Moura MR, Mattoso LHC (2016) Chitosan nanoparticles on the improvement of thermal, barrier, and mechanical properties of high-and low-methyl pectin films. *Food Hydrocolloids* 52:732–740
128. Wu X, Liu Y, Wang W, Han Y, Liu A (2017) Improved mechanical and thermal properties of gelatin films using a nano inorganic filler. *J Food Process Eng*, 40(3), e12469
129. Moreira FK, De Camargo LA, Marconcini JM, Mattoso LH (2013) Nutraceutically inspired pectin–Mg (OH) 2 nanocomposites for bioactive packaging applications. *J Agric Food Chem* 61(29):7110–7119

130. Spoljaric S, Salminen A, Luong ND, Seppälä J (2013) Cross-linked nanofibrillated cellulose: poly (acrylic acid) nanocomposite films; enhanced mechanical performance in aqueous environments. *Cellulose* 20:2991–3005
131. Suganthi S, Vignesh S, Kalyana Sundar J, Raj V (2020) Fabrication of PVA Polymer films with improved antibacterial activity by fine-tuning via organic acids for food packaging applications. *Appl Water Sci* 10(4):1–11
132. Zhang W, Jiang Q, Shen J, Gao P, Yu D, Xu Y, Xia W (2022) The role of organic acid structures in changes of physicochemical and antioxidant properties of crosslinked chitosan films. *Food Packaging Shelf Life* 31:100792
133. Bhatia S, Al-Harrasi A, Al-Azri MS, Ullah S, Makeen HA, Meraya AM, Albratty M, Najmi A, Anwer MK (2022) Gallic acid crosslinked gelatin and casein based Composite films for Food Packaging Applications. *Polymers* 14(19):4065
134. Roy S, Rhim J-W (2022) Genipin-crosslinked gelatin/chitosan-based functional films incorporated with rosemary essential oil and quercetin. *Materials* 15(11):3769
135. Sharma L, Sharma HK, Saini CS (2018) Edible films developed from carboxylic acid cross-linked sesame protein isolate: barrier, mechanical, thermal, crystalline and morphological properties. *J Food Sci Technol* 55:532–539
136. Azeredo HM, Waldron KW (2016) Crosslinking in polysaccharide and protein films and coatings for food contact—A review. *Trends Food Sci Technol* 52:109–122
137. Singh P, Baisthakur P, Yemul OS (2020) Synthesis, characterization and application of crosslinked alginate as green packaging material. *Heliyon*, 6(1)
138. Wen L, Liang Y, Lin Z, Xie D, Zheng Z, Xu C, Lin B (2021) Design of multifunctional food packaging films based on carboxymethyl chitosan/polyvinyl alcohol crosslinked network by using citric acid as crosslinker. *Polymer* 230:124048
139. Picchio ML, Linck YG, Monti GA, Gugliotta LM, Minari RJ, Igarzabal CIA (2018) Casein films crosslinked by tannic acid for food packaging applications. *Food Hydrocolloids* 84:424–434

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.