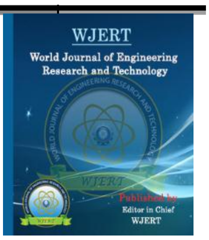
wjert, 2025, Vol. 11 Issue 3, 225-238.
Review Article
ISSN 2454-695X

World Journal of Engineering Research and Technology
WJERT
www.wjert.org
SJIF Impact Factor: 7.029



THE POTENCY OF PHENOLIC COMPOUNDS IN ENHANCING THE PHYSICOCHEMICAL PROPERTIES OF GELATIN FILMS: A REVIEW

Notabo Hlabano[1]*, Londiwe C. Nkiwane[2], Pethile Dzingai[3], Lloyd Njoka Ndlovu[4] and Sithabisiwe Gadlula[5]

[1,2,3,4,5]Department of Fibre and Polymer Materials Engineering, National University of Science and Technology, Box AC 939, Bulawayo, Zimbabwe.

Article Received on 18/01/2025 **Article Revised on 07/02/2025** **Article Accepted on 27/02/2025**

***Corresponding Author**
Notabo Hlabano
Department of Fibre and Polymer Materials Engineering, National University of Science and Technology, Box AC 939, Bulawayo, Zimbabwe.

ABSTRACT

The growing demand for sustainable, biodegradable, and high-performance biomaterials has led to extensive research on natural polymers such as gelatin. Gelatin, a protein-based biopolymer derived from collagen, possesses excellent film-forming abilities, making it a promising material for applications in food packaging, biomedical engineering, and pharmaceuticals. However, its practical applications are often hindered by poor mechanical strength, high water solubility, and low thermal stability, which limit its durability and functionality in diverse environments. Different chemical crosslinking strategies have been widely explored to enhance the structural and physicochemical properties of gelatin-based films. Among various crosslinking agents, phenolic compounds have gained significant attention due to their natural origin, biocompatibility, and multifunctionality. Phenols, such as tannic acid, catechol, ferulic acid, and gallic acid, interact with gelatin through covalent and non-covalent bonding mechanisms, leading to enhanced mechanical strength, reduced water sensitivity, and improved antimicrobial properties. Thus, this review provides a comprehensive analysis of the modifications induced by phenol crosslinking in gelatin-based films. Specifically, it examines the structural alterations resulting from crosslink formation and the physicochemical changes that contribute to their stability and durability. Additionally, these modifications improve antimicrobial properties, making the films suitable for food packaging and biomedical applications. Despite these improvements, challenges remain in optimising crosslinking efficiency, maintaining film flexibility. Future research should therefore focus on improving the balance between flexibility and mechanical strength. By addressing these challenges, phenol crosslinked gelatin films can become more viable alternatives to synthetic polymers, contributing to the advancement of sustainable materials in the biomedical and packaging industries.

KEYWORDS: Gelatin films, Phenolic compounds, Crosslinking, Physicochemical properties, Hydrophobic interactions, Biodegradable films.

1.0 INTRODUCTION

Gelatin is a biopolymer derived from collagen, primarily from animal and fish sources. It is widely used in food packaging, pharmaceuticals, and biomedical applications due to its film-forming ability, biodegradability, and biocompatibility. Gelatin films can be produced from gelatin and these form very important products, finding application in the food, pharmaceutical, and photographic industries as well as in diverse technical applications. Gelatin exists as a mixture of water-soluble protein fragments, composed of the same amino acid sequences as collagen, from which it is derived (Zhang and Wang, 2024). Collagen differs from gelatin in that it contains a triple helical structure, leading to a lower aqueous solubility (Naomi et al., 2021). However, in gelatin, the triple helical structure is lost leading to relatively poor properties, and this limits gelatin uses, for example, in food packaging.

To improve the durability and strength of gelatin films different methods of crosslinking have been reported in the literature. Physical methods include; dehydrothermal treatment, photo-oxidation, segmental orientation, and ultraviolet and gamma radiation (Catalina et al., 2011). Chemical crosslinking uses agents, such as; aldehydes, carbodiimides, epoxy compounds, and acyl azides (Sapuła et al., 2023). These agents chemically form covalent inter and/or intramolecular links between protein chains (Catalina et al., 2011). Although synthetic crosslinking agents are widely used, they are known to be inflammatory and cytotoxic (Jeong et al., 2021). Therefore, this has initiated the need to search for a natural and sustainable material for gelatin crosslinking. Recent studies are now focusing on the use of natural crosslinking agents as a way of producing green, eco-friendly, and sustainable materials (Jeong et al., 2021, Yasin et al., 2022, Yasin et al., 2017).

Phenol crosslinking is a novelty method used to enhance the properties of gelatin films by forming covalent and non-covalent bonds between gelatin molecules and phenolic compounds (e.g., tannic acid, catechol, ferulic acid). This process improves the physicochemical properties of gelatin films. Physicochemical modifications involve changes in chemical interactions and material properties. The formation of covalent bonds enhances the film's resistance to thermal degradation, increases tensile strength, reduces brittleness, and makes the film more durable and flexible.

1.1 Enhancement of Physicochemical Properties of Phenol crosslinked Gelatin films

The physicochemical properties of crosslinked gelatin films are critical in determining the application area of the gelatin films. These properties include mechanical strength, thermal stability, and water resistance. Crosslinking improves these functional attributes by reducing the hydrophilicity of gelatin and increasing its intermolecular interactions (Ahammed et al., 2021, Luo et al., 2022). However, the extent of crosslinking and the method used can significantly impact the film's performance. Thus, understanding the relationship between the crosslinking process and the resulting functional properties of gelatin films is essential for tailoring their application-specific performance, whether for biodegradable packaging, wound dressings, or drug delivery systems.

1.1.1 Water Absorption Properties

Water absorption measures how much water a material can take up when exposed to a liquid for a specific period. Studies have shown that phenol-crosslinked gelatin films offer lower moisture absorption values as compared to non-crosslinked films (Azeredo and Waldron, 2016, Sapuła et al., 2023). The incorporation of crosslinking agents decreases water absorption by increasing the film’s cohesive structure thereby reducing free volume spaces between polymer chains and lowering the free volume for moisture absorption (Martucci et al., 2015). Also, the formation of hydrophobic interactions between gelatin amino acids and phenol hydroxyl and carbonyl groups contributes to lower water absorption values (Liu et al., 2019).

Crosslinking at moderate phenol concentrations (0.5- 5%) has been shown to proffer better water interaction properties on the films which allows them to better withstand application conditions especially when used in humid conditions (Yasin et al., 2017). Gelatin films crosslinked with phenol concentrations below 0.5% tend to show the highest water absorption as compared to other crosslinked samples due to an increase in several gaps/voids in its structure as well as the presence of unbonded amine groups, carbonyl group, and ethyl groups within the gelatin amino acids due to low phenol concentrations. These free unreacted groups provide an easy channel by which water can penetrate the gelatin molecular structure.

Water absorption values decrease with an increase in phenol concentration as crosslinking enables the formation of hydrogen bonds between gelatin amino acids and phenolic compounds and this reduces the amount of free hydrogen atoms available for bonding with water molecules (Montazerian et al., 2023). This reduction is more prominent at moderate phenol concentration and this indicates an increase in the density of crosslinks formed between the phenolic compounds and gelatin amino acids. High crosslinking density results in a reduction in free volume within the film leading to low water penetration and ultimately low water absorption (Luo et al., 2022).

1.1.2 Tensile Strength

Stress-strain curves show that pure gelatin films have a brittle fracture whereas phenol-crosslinked gelatin films have a ductile fracture (Liu et al., 2023, Martucci et al., 2011, Chen et al., 2022). Brittleness is caused by the interaction between polymer chains of gelatin through hydrogen bonding (Chen et al., 2022). The intrusion of phenol into the gelatin molecular structure allows for hydrogen bonds to take place between phenol and gelatin and this reduces the intermolecular bonds formed between amino acids (Chen et al., 2022). Literature reveals that the formation of free space and discontinuities within the gelatin matrix is caused by the intrusion of high molecular weight phenol crosslinkers (such as tannins and lignin) or poor interaction/compatibility between phenol and gelatin contribute to this effect (Aadil et al., 2016, Catalina et al., 2011). Thus, phenol reduces brittleness and promotes flexibility and chain mobility. According to Jayachandra et al., 2022, brittleness is one of the main limitations of gelatin-based films and has been shown to reduce their application areas.

Literature shows that the tensile strength of gelatin films ranges between 0.70-51.68MPa (Martucci et al., 2015, Rawdkuen et al., 2020, Suderman et al., 2018). The mechanical properties of gelatin are associated with the triple helix content (Said and Sarbon, 2022). At optimum (0.5 to 5%wt. per 100g of gelatin) phenol concentration, there is a reduction in free space within the gelatin matrix due to strong covalent interactions formed between the side chains of amino groups (C-N and C-S) and hydrogen bonding between the amine groups and the phenol hydroxyl and carbonyl groups of phenolic compounds (Teixeira-Costa and

Andrade, 2021, Ordoñez et al., 2022). This results in the formation of a denser, stiffer, and more tightly packed structure (Choi et al., 2018).

According to Inyoung Choi et al., 2018, the addition of phenol in excess increases the molecular mobility within gelatin films due to grafting and branching reactions. This causes a plasticising effect which ensures that the strength values are not improved but are kept close to those of the non-crosslinked gelatin film. Moreover, due to a lack of gelatin reactive sites, phenol quinones form oligomers with one another, occupying free space within the gelatin matrix, and disturbing the orderly arrangement of gelatin chains (Schefer et al., 2021). Therefore, this increases the flexibility of gelatin chains leading to no significant changes in tensile strength values after crosslinking but producing the flexibility needed in gelatin films.

The addition of polyphenolic compounds has been shown to cause a reduction rather than an increase in crystallinity. This is in agreement with findings from Aadil et al., 2016, during a study of acacia lignin-gelatin films where it was found that tensile strength decreased with increasing lignin concentration. It was therefore concluded that lignin has a plasticising effect on gelatin films which caused a reduction in molecular attraction forces between polymer chains. Catalina et al., 2011, also found that the intrusion of phenol molecules led to an increase in free volume which causes a plasticising effect.

However, another study done by Peña et al., 2010 found that the addition of 10 wt.% tannins (weight of tannin to the weight of dry gelatin) results in the production of gelatin with high tensile strength and modulus of 120 and 4200 MPa, respectively. Also, another study conducted by Yasin et al., 2017 showed that; the polyphenol concentration of between 1-5ml/100g dry gelatin produced better properties.

1.1.3 Elongation at Break (EAB) and Young's Modulus (E)

High elongation values ranging from 2.10-561% have been found after crosslinking gelatin with natural extracts like peppermint, cinnamon, lemon grass, basil, rosemary, et cetera (Yasin et al., 2017, Martucci et al., 2015, Rawdkuen et al., 2020). The values are in line with the biodegradable plastic SNI 7818:2014 standard of 400 – 1220% elongation values. Natural extracts reduce the intermolecular forces within the gelatin matrix and lead to the production of more flexible films (Benjakul et al., 2016). Moreover, these extracts exhibit a plasticising effect that increases free volume, enhances great mobility, and has high elongation values (Tongnuanchan et al., 2016). According to Schefer et al., 2021, high elongation values might be due to the formation of new interactions between phenolic compounds of plant extracts with side chains of gelatin amino acids which leads to high extensibility.

Young's modulus in gelatin crosslinked films has been shown to increase directly proportional to TS and inversely proportional to EAB (Ashrafi et al., 2023). This is because films with high elongation values are more prone to plastic deformation than films with low elongation values. Crosslinking of gelatin amino acids with either synthetic or natural crosslinking agents have been shown to produce a plasticising effect (Vieira et al., 2011). This causes the elongation values to increase, and the young's modulus to decrease. Thus, it should be noted that attaining the high percentage elongation values means a reduction in strength values. Thus, before the production of bioplastics, it is necessary to know in advance whether the objective of making the gelatin film is to obtain a higher elongation value or tensile strength as the two values are inversely proportional.

1.1.4 Thermal Stability

Differential Scanning Calorimetry (DSC) is used to determine the glass transition temperature (Tg), the melting temperature, the crystallisation temperature (Tc), and changes in heat enthalpies (Zhao et al., 2017). Tg of gelatin films ranges from 20- 84.6°C (Bonilla et al., 2017, Mukherjee and Rosolen, 2013). At their glass transition temperature, the mobility of gelatin occurs due to a decrease in intermolecular forces within the polymer chain.

According to Yan-Ping et al., 2016 and Fernandos et al., 2022, the melting of gelatin occurs between 60°C and 105°C. The thermal stability of gelatin films is associated with the amino acid content, that is; high amino acid content increases the coil-helix transition temperature. Coil-helix transition occurs as a result of breakage of hydrogen bonds. Phenol crosslinking has been shown to cause a positive shift in the melting temperature, that is, crosslinked films have melting temperatures around 102-167°C which is 59% higher than that of non-crosslinked films (Said and Sarbon, 2022). The increase in melting temperature after crosslinking is a result of the dense polymer structure formed due to crosslinking (Arfat, 2017). However, it has been shown that some crosslinking agents like plant extracts and some essential oils can cause discontinuity in the film matrix, and this can lower the energy required to break the polymer chains and melting temperature (Silva-Weiss et al., 2013).

The DSC thermogram in Figure 1 shows the glass transition and the melting temperature of polyphenolic compounds. According to Burton Sickler, 2019, a material exhibiting both the glass transition curve as well as the melting temperature curve is said to be semi-crystalline. Thus, phenolics are semi-crystalline.

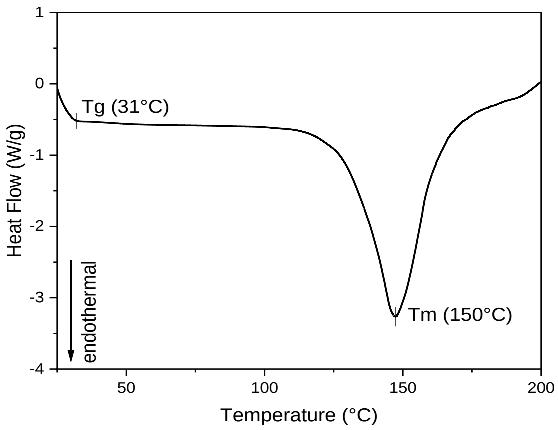


Figure 1: Thermogram of a Plant Phenolic Compound (Hlabano et al., 2020).

Phenolic compounds have an endothermic peak at 150°C and this is in line with the temperature found by Ji-Sang Kim et al., 2020 during a study of four prominent phenolic compounds. Several studies have shown that the disappearance of this peak after crosslinking is an indication of a successful complex formation whereas a partial complexation is shown by a shift to lower temperatures (Venezia et al., 2021, Liu et al., 2019). Possible reasons for partial complexation/lack of thermodynamic miscibility may be due to the crosslinking method used. The best approach can be the use of enzyme-assisted crosslinking (e.g. laccase oxidase) to direct the crosslinking process.

DSC thermograms have revealed three major peaks in phenol-crosslinked gelatin films. The first peak is related to the second-order transition of the amorphous part of gelatin and phenols, that is; the glass transition (Tg). This is followed by the exothermic crystallisation temperature (Tc) peak and then the first endothermic melting temperature (Tm) peak. The endothermic peak denotes a thermodynamic transition in the gelatin structure which destroys the gelatin-ordered molecular structure due to the breakage of hydrogen bonds and melting of the crystalline gelatin (Wang et al., 2021). Sometimes, due to poor fusion between gelatin and phenol, a fourth peak can be seen in some thermograms (Wang and Xiong, 2021, Liu et al., 2022).

Tc is associated with loss of heat as polymer chains rearrange themselves orderly whereas during the first-order transition gelatin polypeptide chain changes from a helical structure to a random coil (Bastarrachea et al., 2011, Hager et al., 2012, Aadil et al., 2016). The first-order endothermic peak shows the melting temperature of phenol-crosslinked gelatin film. This peak is evidence of the interaction and miscibility of phenolic compounds and amino acids of gelatin. The effect of crosslinking on the gelatin structure is clearly shown on the gelatin endothermic peak in DSC thermograms.

After crosslinking, the endothermic peaks can shift or become attenuated suggesting the possible formation of hydrophobic interactions between gelatin and phenolic compounds. Simone et al. (2021) and Catalina et al. (2011) highlighted that a shift of the endothermic peak to a lower temperature might be due to the intrusion of phenolic compounds into the gelatin structure leading to the creation of free volume which results in a decrease in orderly arrangement of gelatin polymers leading to a decrease in melting temperature. However, optimum phenolic content has been shown to proffer an increase in stability of the gelatin crosslinked films and this results in an increase in thermal stability for instance Wang et al. (2021) observed an increase in melting temperature by 5°C after crosslinking whey protein with ferulic acid. In another study, Hazmah et al., 2024, observed a 14% increase in melting temperature after crosslinking gelatin with plant phenol. These observations show that the incorporation of phenolic compounds into the gelatin matrix results in more thermally stable gelatin films.

1.1.5 Biodegradation

Phenol-modified gelatin films degrade more slowly than non-crosslinked gelatin but remain environmentally friendly compared to synthetic plastics. The biodegradation of phenol crosslinked gelatin films has been shown to range between 18-25% after 3 days of burial (Martucci et al., 2015, Martucci and Ruseckaite, 2009). The addition of natural crosslinking agents has been shown to reduce biodegradability to less than 20% after a 3-day burial. This is because crosslinking agents increase the compactness of the structure, lower the free volume for moisture penetration, and increase the molecular weight of the gelatin matrix thus reducing the biodegradability rate (Martucci and Ruseckaite, 2009, Bakry et al., 2017).

A high biodegradation rate of up to 55% within a 3-day window period has been observed in gelatin films and is associated with the presence of water-soluble proteins (Rostini et al., 2019). High degradation levels are associated with the content of hydroxyproline in the gelatin matrix as this amino acid easily bonds with water molecules in the soil thus providing an easy channel through which water may enter the film's molecular structure (Avena- Bustillos et al., 2006). High moisture content has also been shown to increase microbial growth and this causes an increase in biodegradability. Research has shown that intrusion of phenol into the gelatin matrix can disrupt the order in the gelatin structure and increase the free volume which allows for increased penetration of water and soil microorganisms which are the factors necessary for degradation to occur (Ahmad et al., 2012). This can be represented by the biodegradation curves which are steep and parallel to one another showing relatively fast degradation.

However, gelatin films with optimum phenol concentration have shown the lowest degradation levels with most films degrading after more than 10 days (Kola and Carvalho, 2023). The low degradation values might be due to the high concentration of phenolic compounds in the gelatin structure which impede microbial degradation action due to the antimicrobial nature of phenolics (Maroyi, 2017). However, due to humid soil, demineralization of some phenolic compounds can occur after 10 days leading to an increase in microbial attack and high degradation levels. Thus, the slow degradation rate in phenol crosslinked gelatin films might be caused by the highly dense internal structure of the films. The dense network structure is a result of covalent and non-covalent interactions between gelatin and phenolic compounds which allows for slow degradation. The other reason could be due to the antimicrobial properties of phenol which hinders the biodegradation action by soil microorganisms (Maroyi, 2017). Based on these observations, gelatin crosslinked with polyphenolic compounds can be classified under films that are readily biodegradable as degradation occurs in less than 3 months. Thus, the films can be utilised as a biodegradable and safe material in packaging, tissue engineering, drug delivery, et cetera.

2.0 CONCLUSION

This review provides a comprehensive analysis of gelatin-based films, with a particular focus on their physicochemical modifications through phenolic crosslinking. Studies have indicated that cross-linking at low phenol concentrations (<0.5%) increased the free volume in the gelatin matrix and this led to high elongation values, low tensile strength, and high water absorption as compared to films produced with optimum phenol concentration (0.5% to 5%). Moreover, the crosslinked films, at optimum phenol concentrations present better thermal, mechanical, and water absorption properties than the non-crosslinked films, which allows the films to better withstand different application conditions. The lack of gelatin reactive groups at high phenol concentration leads to an increase in free volume as oxidised phenol forms oligomers/grafts on the surface of gelatin polymer chains thus increasing polymer mobility and elongation values and ultimately reducing brittleness.

These findings show that polyphenolic compounds can improve the properties of gelatin films by acting both as a crosslinker to; improve the structural rigidity of gelatin films and a plasticiser for improving the elongation properties of gelatin. However, challenges remain in optimising crosslinking efficiency. Future research should therefore focus on improving the balance between flexibility and mechanical strength. By addressing these challenges, phenol crosslinked gelatin films can become more viable alternatives to synthetic polymers, contributing to the advancement of sustainable materials in various industries.

3.0 REFERENCES

1. AADIL, K. R., BARAPATRE, A. & JHA, H. Synthesis and characterization of Acacia lignin-gelatin film for its possible application in food packaging. Bioresources and Bioprocessing, 2016; 3: 1-11.
2. AHAMMED, S., LIU, F., WU, J., KHIN, M. N., YOKOYAMA, W. H. & ZHONG, F. Effect of transglutaminase crosslinking on solubility property and mechanical strength of gelatin-zein composite films. Food Hydrocolloids, 2021; 116: 106649.
3. AHMAD, M., BENJAKUL, S., PRODPRAN, T. & AGUSTINI, T. W. Physico-mechanical and antimicrobial properties of gelatin film from the skin of unicorn leatherjacket incorporated with essential oils. Food hydrocolloids, 2012; 28: 189-199.
4. ARFAT, Y. A. Plasticizers for biopolymer films. Glass transition and phase transitions in food and biological materials, 2017; 159-182.
5. ASHRAFI, A., BABAPOUR, H., JOHARI, S., ALIMOHAMMADI, F., TEYMORI, F., NAFCHI, A. M., SHAHRAI, N. N., HUDA, N. & ABEDINIA, A. Application of poultry gelatin to enhance the physicochemical, mechanical, and rheological properties of fish gelatin as alternative mammalian gelatin films for food packaging. Foods, 2023; 12: 670.
6. AVENA- BUSTILLOS, R., OLSEN, C., OLSON, D., CHIOU, B.-S., YEE, E., BECHTEL, P. & MCHUGH, T. Water vapor permeability of mammalian and fish gelatin films. Journal of food science, 2006; 71: E202-E207.
7. AZEREDO, H. M. & WALDRON, K. W. Crosslinking in polysaccharide and protein films and coatings for food contact–A review. Trends in Food Science & Technology, 2016; 52: 109-122.
8. BAKRY, N. F., ISA, M. & SARBON, N. M. Effect of sorbitol at different concentrations on the functional properties of gelatin/carboxymethyl cellulose (CMC)/chitosan composite films. International Food Research Journal, 2017; 24.

9. BASTARRACHEA, L., DHAWAN, S. & SABLANI, S. S. Engineering properties of polymeric-based antimicrobial films for food packaging: a review. Food Engineering Reviews, 2011; 3: 79-93.
10. BENJAKUL, S., NAGARAJAN, M. & PRODPRAN, T. 2016. Films and coatings from collagen and gelatin. Edible films and coatings. CRC Press.
11. BONILLA, J., BITTANTE, A. M. Q. & SOBRAL, P. J. Thermal analysis of gelatin–chitosan edible film mixed with plant ethanolic extracts. Journal of Thermal Analysis and Calorimetry, 2017; 130: 1221-1227.
12. CATALINA, M., ATTENBURROW, G. E., COT, J., COVINGTON, A. D. & ANTUNES, A. P. M. Influence of crosslinkers and crosslinking method on the properties of gelatin films extracted from leather solid waste. Journal of Applied Polymer Science, 2011; 119: 2105-2111.
13. CHEN, L., QIANG, T., CHEN, X., REN, W. & ZHANG, H. J. Gelatin from leather waste to tough biodegradable packaging film: One valuable recycling solution for waste gelatin from leather industry. Waste Management, 2022; 145: 10-19.
14. CHOI, I., LEE, S. E., CHANG, Y., LACROIX, M. & HAN, J. Effect of oxidized phenolic compounds on cross-linking and properties of biodegradable active packaging film composed of turmeric and gelatin. Lwt, 2018; 93: 427-433.
15. HAGER, A.-S., VALLONS, K. J. & ARENDT, E. K. Influence of gallic acid and tannic acid on the mechanical and barrier properties of wheat gluten films. Journal of agricultural and food chemistry, 2012; 60: 6157-6163.
16. HLABANO, N., NKIWANE, L. C., DZINGAI, P. & GADLULA, S. Proximate analysis and evaluation of total phenolic compounds in Azanza garckeana fruit for use as gelatin crosslinking agent. Zimbabwe Journal of Science and Technology, 2020; 15: 157-166.
17. JEONG, C. H., YUNE, J. H., KWON, H. C., SHIN, D.-M., SOHN, H., LEE, K. H., CHOI, B., KIM, E. S., KANG, J. H. & KIM, E. K. In vitro toxicity assessment of crosslinking agents used in hyaluronic acid dermal filler. Toxicology in Vitro, 2021; 70: 105034.
18. KOLA, V. & CARVALHO, I. S. Plant extracts as additives in biodegradable films and coatings in active food packaging. Food Bioscience, 2023; 54: 102860.
19. LIU, J., YONG, H., YAO, X., HU, H., YUN, D. & XIAO, L. Recent advances in phenolic–protein conjugates: Synthesis, characterization, biological activities and potential applications. RSC advances, 2019; 9: 35825-35840.

20. LIU, Y., SAMEEN, D. E., AHMED, S., WANG, Y., LU, R., DAI, J., LI, S. & QIN, W. Recent advances in cyclodextrin-based films for food packaging. Food Chemistry, 2022; 370: 131026.
21. LUO, Q., HOSSEN, M. A., ZENG, Y., DAI, J., LI, S., QIN, W. & LIU, Y. Gelatin-based composite films and their application in food packaging: A review. Journal of Food Engineering, 2022; 313: 110762.
22. MAROYI, A. 2017. Azanza garckeana fruit tree: phytochemistry, pharmacology, nutritional and primary healthcare applications as herbal medicine: a review.
23. MARTUCCI, J. F., GENDE, L. B., NEIRA, L. & RUSECKAITE, R. A. Oregano and lavender essential oils as antioxidant and antimicrobial additives of biogenic gelatin films. Industrial Crops and products, 2015; 71: 205-213.
24. MARTUCCI, J. F. & RUSECKAITE, R. A. Biodegradation of three-layer laminate films based on gelatin under indoor soil conditions. Polymer Degradation and Stability, 2009; 94: 1307-1313.
25. MONTAZERIAN, H., SAMPATH, R. R., ANNABI, N., KHADEMHOSSEINI, A. & WEISS, P. S. Polyphenolic gelatin-based bioadhesives. Accounts of Materials Research, 2023; 4: 627-640.
26. MUKHERJEE, I. & ROSOLEN, M. Thermal transitions of gelatin evaluated using DSC sample pans of various seal integrities. Journal of Thermal Analysis and Calorimetry, 2013; 114: 1161-1166.
27. NAOMI, R., BAHARI, H., RIDZUAN, P. M. & OTHMAN, F. Natural-based biomaterial for skin wound healing (Gelatin vs. collagen): Expert review. Polymers, 2021; 13: 2319.
28. ORDOÑEZ, R., ATARÉS, L. & CHIRALT, A. Biodegradable active materials containing phenolic acids for food packaging applications. Comprehensive Reviews in Food Science and Food Safety, 2022; 21: 3910-3930.
29. RAWDKUEN, S., FASEHA, A., BENJAKUL, S. & KAEWPRACHU, P. Application of anthocyanin as a color indicator in gelatin films. Food Bioscience, 2020; 36: 100603.
30. ROSTINI, I., PRATAMA, R. I. & ROCHIMA, E. Characterization of bioplastic packaging from tapioca flour modified with the addition of chitosan and fish bone gelatin. World Scientific News, 2019; 135.
31. SAID, N. S. & SARBON, N. M. Physical and mechanical characteristics of gelatin-based films as a potential food packaging material: A review. Membranes, 2022; 12: 442.

32. SAPUŁA, P., BIALIK-WĄS, K. & MALARZ, K. Are natural compounds a promising alternative to synthetic cross-linking agents in the preparation of hydrogels? Pharmaceutics, 2023; 15: 253.
33. SCHEFER, S., OEST, M. & ROHN, S. Interactions between phenolic acids, proteins, and carbohydrates—Influence on dough and bread properties. Foods, 2021; 10: 2798.
34. SILVA-WEISS, A., IHL, M., SOBRAL, P. D. A., GÓMEZ-GUILLÉN, M. & BIFANI, V. Natural additives in bioactive edible films and coatings: functionality and applications in foods. Food Engineering Reviews, 2013; 5: 200-216.
35. SUDERMAN, N., ISA, M. & SARBON, N. Characterization on the mechanical and physical properties of chicken skin gelatin films in comparison to mammalian gelatin films. IOP conference series: Materials science and engineering, IOP Publishing, 2018; 012033.
36. TEIXEIRA-COSTA, B. E. & ANDRADE, C. T. Natural polymers used in edible food packaging—History, function and application trends as a sustainable alternative to synthetic plastic. Polysaccharides, 2021; 3: 32-58.
37. TONGNUANCHAN, P., BENJAKUL, S., PRODPRAN, T., PISUCHPEN, S. & OSAKO, K. Mechanical, thermal and heat sealing properties of fish skin gelatin film containing palm oil and basil essential oil with different surfactants. Food Hydrocolloids, 2016; 56: 93-107.
38. VENEZIA, V., AVALLONE, P. R., VITIELLO, G., SILVESTRI, B., GRIZZUTI, N., PASQUINO, R. & LUCIANI, G. Adding humic acids to gelatin hydrogels: a way to tune gelation. Biomacromolecules, 2021; 23: 443-453.
39. VIEIRA, M. G. A., DA SILVA, M. A., DOS SANTOS, L. O. & BEPPU, M. M. Natural-based plasticizers and biopolymer films: A review. European polymer journal, 2011; 47: 254-263.
40. WANG, X., HOU, M., LIU, X., YUE, O. & ZHENG, M. Feasibility study of gelatin preparation from the bioinspired collagen aggregates by a “two-step” facile degradation method. ACS Applied Bio Materials, 2021; 4: 2363-2372.
41. WANG, Y. & XIONG, Y. L. Physicochemical and microstructural characterization of whey protein films formed with oxidized ferulic/tannic acids. Foods, 2021; 10: 1599.
42. YASIN, A., REN, Y., LI, J., SHENG, Y., CAO, C. & ZHANG, K. Advances in hyaluronic acid for biomedical applications. Frontiers in Bioengineering and Biotechnology, 2022; 10: 910290.

43. YASIN, H., BABJI, A. S. & NORRAKIAH, A. S. Modification of chicken feet gelatin with aqueous sweet basil and lemongrass extract. LWT, 2017; 77: 72-79.
44. ZHANG, Y. & WANG, J. Current status and prospects of gelatin and its derivatives in oncological applications. International Journal of Biological Macromolecules, 2024; 133590.
45. ZHAO, D., LIU, G., SUN, J. & WANG, L. Enthalpy of phase transition of isonicotinic acid. Chinese Journal of Chemical Engineering, 2017; 25: 971-975.