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Comparative effect of different plasticizers on physicochemical properties of hydroxypropyl methyl cellulose (HPMC)- based films appropriate for gilthead seabream packaging

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ABSTRACT

The selection of adequate plasticizers to synthesize biopolymer biodegradable and edible films for food packaging is crucial to develop materials with appropriate barriers, mechanical and physicochemical properties. The aim of the study was to develop hydroxypropyl methyl cellulose (HPMC) based films with hydrophilic and hydrophobic plasticizers and evaluate their effectiveness as green packaging materials for gilthead seabream fillets. Mechanical properties, water barrier, surface hydrophobicity, optical and UV–visible barrier properties were determined. The films produced were transparent with excellent optical appearance and good preventive ability against UV radiation. HPMC based films with glycerol as plasticizer were more compact and had lower thickness (45.43 ± 3.33 μm) and higher young's modulus, indicating stiffer, less flexible films (1613.22 ± 492.88 MPa). In contrast, films plasticized with oleic acid had the highest elongation at break (30.35 ± 4.21 %), indicating greater flexibility. The films with glycerol were hydrophilic (contact angle equal to $81.47\pm6.65^\circ$) while the films with fatty acids (oleic and linoleic acid) were hydrophobic (contact angle $> 90^\circ$). The hydrophobic films had also better water barriers compared to films with glycerol. All tested packaging materials resulted in similar preservative effect on packed gilthead seabream fillets, leading in shelf life 7–8 days at 2 °C. The results of the study show the potential of the developed biodegradable films to replace the conventional synthetic petroleum based materials in fresh fish packaging.

1. Introduction

Food packaging plays a crucial role in preserving the quality and safety of food by functioning as a barrier to the transfer of moisture, aroma, and gases. Additionally, it serves as an external protective layer against microorganisms and other contaminants (Cheng et al., 2024). Petroleum based plastics, including polyethylene, polypropylene, and polystyrene, have been widely utilized for decades due to their low cost, durability, and favorable mechanical properties. However, the extensive use of these non-biodegradable materials has raised significant environmental concerns (Cheng et al., 2022).

Sustainable packaging materials have been investigated as alternatives to conventional polymers. Derived from biodegradable (and in some cases edible) raw compounds, these materials can either be safely consumed with food or decomposed through chemical, physical, or enzymatic processes without releasing harmful environmental pollutants (Amin et al., 2021). They are typically synthesized from biological macromolecules such as polysaccharides, proteins, and lipids (Suderman et al., 2018).

Polysaccharides, composed of >10 monosaccharide units linked by glycosidic bonds ($\alpha-1,4$-, $\beta-1,4$-, or $\alpha-1,6$) are the most abundant macromolecules in the biosphere and are primarily sourced from plants, animals, and microorganisms (Marasinghe et al., 2024). In packaging applications, high molecular weight polysaccharides are used for their

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ability to form dense, networked films through intra- and intermolecular hydrogen bonding, providing adequate mechanical strength (Wu et al., 2024). These films exhibit excellent optical clarity and effective gas barrier properties due to their compact structure. However, their inherent hydrophilicity leads to high water vapor permeability (M. Wang et al., 2024). To address this limitation, hydrophobic compounds such fatty acids are incorporated into the film forming solution (Zubair et al., 2021).

Cellulose, the most abundant polysaccharide, is derived from plants, microorganisms, animals, and certain algae. Its exceptional structural, chemical, mechanical and thermal properties are attributed to its nanofibrillar three-dimensional structure (Jang et al., 2023). Structurally, cellulose is a linear polymer of d-anhydroglucopyranose ($C_6H_{11}O_5$) units-glucose monomers linked into repeating cellobiose units via β−1, 4-glycosidic bonds. Each cellulose chain contains both crystalline and amorphous regions and is highly hydrophilic due to numerous hydroxyl groups (Zugenmaier, 2001). However, its inherent moisture sensitivity and poor solubility in water and most solvents limit its direct application as a biocompatible polymer. To overcome this limitations, chemical modification of the hydroxyl groups is employed to produce cellulose derivatives with improved functionality (Seddiqi et al., 2021).

Hydroxypropyl methyl cellulose (HPMC) (Fig. 1) is a cellulose derivative in which hydroxyl groups are partly methylated and 2-hydroxypropylated, forming ether linkages with the cellulose backbone. HPMC is a non-ionic, water soluble, enzyme resistant polymer, exhibiting stability across a pH range of 3 to 11. Its gel forming capacity arises from hydrophobic interactions that create crosslinks between polymer chains, a property influenced by both molecular weight and the degree of substitution on the cellulose backbone (Arévalo-Pérez et al., 2020). Although HPMC exhibits excellent film-forming properties when plasticizer are incorporated into its matrix, its inherent brittleness hinders the formation of flexible and continuous films in their absence. Moreover, its pronounced hydrophilicity necessitates modification to enhance functionality. To improve the water barrier properties of HPMC-based edible films, hydrophobic compounds such as waxes have been investigated (Hosseini et al., 2023; Jiménez et al., 2010)

To enhance functionality, additional compounds such as plasticizers are incorporated into edible film forming solutions. Plasticizers improve the mechanical properties and cohesiveness of the films, affecting their strength and uniform structure. These low-volatility molecules are added to the polymer matrix to modify the film functional properties, increasing their extensibility, flexibility, elasticity, and rigidity. Common plasticizers studied include polyols such as glycerol, sorbitol, mannitol and xylitol, and fatty acids (Suderman et al., 2018).

Glycerol, a sugar alcohol with three hydroxyl groups, is highly soluble in water. Literature indicates that each glycerol molecule forms 5.68±1.51 hydrogen bonds, which are approximately linear. The hydrogen bonding network between in glycerol is more disordered than in pure water, allowing glycerol and water to mix efficiently without forming ice or glycerol crystals. This property makes glycerol an ideal plasticizer for water-based solutions (Towey et al., 2011). In addition to glycerol, other plasticizers such as fatty acids have also been explored to modify the mechanical and barrier properties of edible films. Free fatty acids are components of lipids, consisting of carbon and hydrogen chains with a methyl group at one end and a carboxylic group at the other. They are classified into two categories: saturated and unsaturated fatty acids. Oleic acid and linoleic acid are unsaturated fatty acids with 18 carbon atoms. Oleic acid is a monounsaturated omega-9 fatty acid, while linoleic acid is a polyunsaturated, omega-6 fatty acid (Balasubramaniam et al., 2020; Karacor & Cam, 2015). The chemical structures of (a) glycerol, (b) oleic acid and (c) linoleic acid are showed in Fig 2.

Fish and fish products have a limited shelf life due to the rapid growth of spoilage bacteria during storage. Several studies have examined the use of edible packaging materials to preserve seafood quality (Gómez-Estaca et al., 2010; Günlü & Koyun, 2013; Kumar et al., 2022; Remya et al., 2016; Rezaei & Shahbazi, 2018). However, limited studies have assessed the effect of edible packaging materials on gilthead seabream (*Sparus aurata*).

Gilthead seabream is one of the most important marine species cultivated in Mediterranean countries, with an estimated annual production of approximately 258,754 tons/year (Mhalhel et al., 2023). It is highly demanded globally due to its desirable characteristics, including high quality flesh, appealing taste, and distinctive aroma (Mendes, 2019). According to FAO (2021), rising consumer demand over the past two decades has driven the aquaculture sector to significantly increase production to meet international markets needs. Leading producers, i.e. Greece, Spain, Turkey, Tunisia and Egypt, account for over 90 % of the global production. The biochemical composition of gilthead seabream makes it highly susceptible to spoilage, a characteristic shared with many other fish species. Spoilage during storage is primarily caused by Specific Spoilage Organisms (SSO), whose metabolic activity accelerates the degradation of sensory and nutritional quality, rendering the product unsuitable for consumption. Fish spoilage is a major economic and environmental issue, with nearly 30 % of fish products discarded before reaching consumers (Anagnostopoulos et al., 2023). Studies show that storage conditions, particularly temperature and packaging methods, significantly affect the shelf life and microbiological profile of gilthead seabream fillets (Anagnostopoulos et al., 2023; Carrascosa et al., 2015;

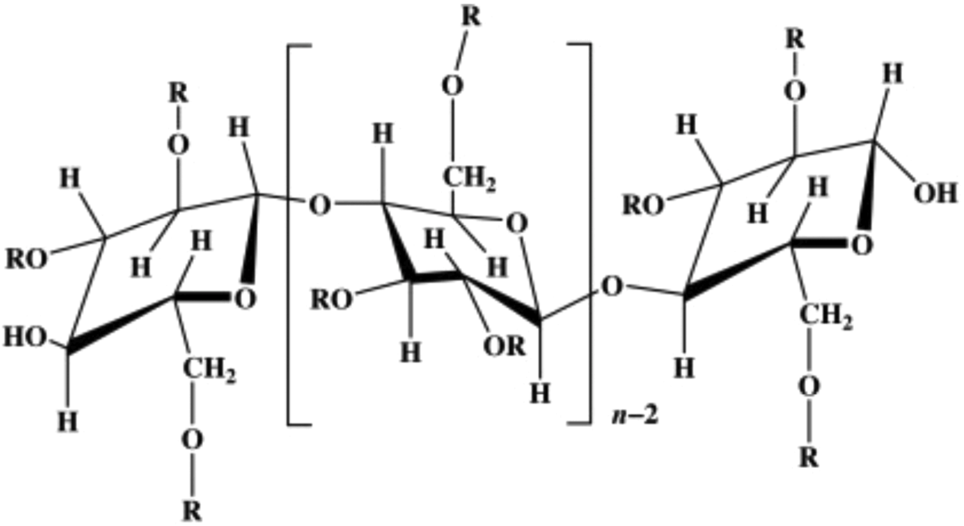

Fig. 1. Chemical structure of hydroxypropyl methyl cellulose (HPMC) where $R = H$, -CH_3 or –$(OCH_2CHCH_3)_xOH$ (Deshmukh et al., 2017).

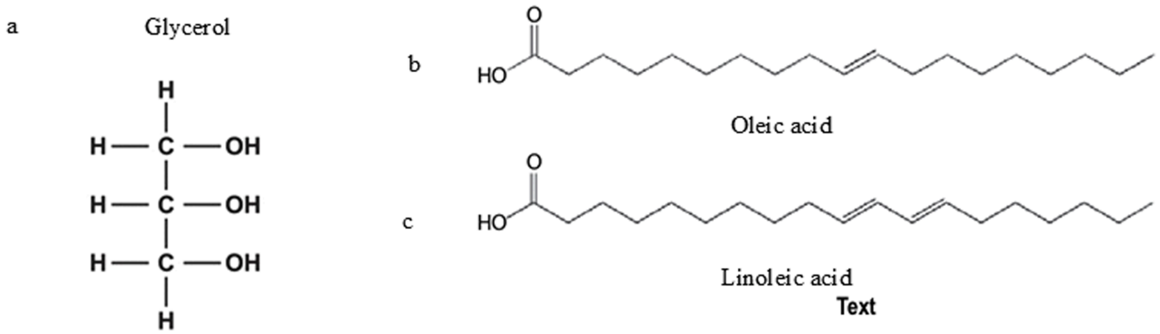

Fig. 2. Chemical structure of molecules of (a) glycerol, (b) oleic acid and (c) linoleic acid.

Tryfinopoulou et al., 2002). Effective storage and packaging strategies are crucial for preserving the quality and marketability of this key species in the Mediterranean seafood industry.

Previous studies have focused on enhancing the barrier and mechanical properties of HPMC based films by incorporating plasticizers (Laboulfie et al., 2013; Malik et al., 2022; Nguyen et al., 2021; Sarignat et al., 2005; Zhang et al., 2018). Glycerol, typically used at concentrations ranging from 10 to 50 wt.% remains the most common plasticizer in these films, although limited studies have explored the effects of saturated and unsaturated fatty acids (e.g. stearic, palmitic, oleic acid and linoleic acids) (Brogly et al., 2024; Fahs et al., 2010; Jiménez et al., 2010; Laboulfie et al., 2013). There is increasing market interest in replacing conventional plasticizers with biodegradable alternatives, particularly in combination with biopolymers (De Souza & Gupta, 2024). Key factors in plasticizer selection include compatibility with the polymer and plasticization efficiency. For food packaging, migration and toxicity concerns are crucial, with natural plasticizers generally exhibiting low toxicity (Vlacha et al., 2016). Replacing glycerol with hydrophobic compounds in HPMC films may not only improve plasticization but also enhance water barrier properties. To our knowledge, no studies have yet compared the effects of oleic acid and linoleic acid as plasticizers in HPMC films for real food systems. In this study, glycerol was used as a reference plasticizer for direct comparison with the two fatty acids, and the resulting film properties were evaluated.

This study aimed to investigate different plasticization systems for HPMC films by evaluating the effect of on the effects of hydrophilic (glycerol) and hydrophobic (oleic and linoleic acid) plasticizers on the HPMC matrix. The resulting films were compared for their physicochemical and mechanical properties and tested for their potential as packaging materials for fresh gilthead seabream (*Sparus aurata*) fillets stored at 2 °C. The shelf life of the fish was determined through microbial growth monitoring. The overall objective was to identify the most suitable plasticizer and evaluate its impact on the preservation of packed fresh gilthead seabream fillets.

2. Materials and methods

2.1. Materials

Hydroxypropyl methylcellulose (hydroxypropyl 5–8 %, methoxy 28–30 %) (2.6–5.6 Pa-s, 2 % in H_2O 20 °C) was supplied from ACEF SPA (Piacenza, Italy). Linoleic acid 60 % (CAS No 60–33–3) were purchased from ThermoFisher Scientific and oleic acid (CAS No 112–80–1) were purchased from penta chemicals unlimited.

2.2. Synthesis of films

The films were synthesized according to solvent casting method. 2 % w/v of HPMC was dissolved into distilled water and stirring at 80 °C for 1 h using magnetic stirrer. Glycerol, linoleic acid and oleic acid (30 % w/w) was used as plasticizers and were added after the temperature was decreased at 30 °C. 25 mL of each solution was poured into plastic petri dishes with a diameter of 14 mm and dried at room temperature for 24 h. The films were stored until their analysis at saturated sodium bromide (RH 58 %) at room temperature.

2.3. Characterization of films

2.3.1. Surface morphology

The surface morphology of the films was examined using a field emission scanning electron microscope (NovaNano SEM 450, FEI, USA) in a low vacuum mode (80 kPa) with an acceleration voltage of 10 kV. Film samples were cut (2 × 2 mm^2) to mount on stainless steel stubs with double-sided tape (Bigi et al., 2021).

2.3.2. Fourier-transform infrared (FT-IR) spectroscopy

The FTIR spectra of the films were obtained using an ATR/FT-IR spectrometer (Alpha, Bruker Optik GmbH, Ettingen, Germany). Each spectrum was recorded from the top and bottom of the same sample in the infrared region between 4000–400 cm^{-1} at a spectral resolution of 4 cm^{-1} by accumulating 64 scans. Each measurement was performed in triplicate (Bigi et al., 2021).

2.3.3. Thickness and mechanical properties

Before the analysis, films were stored in a desiccator for at least one week to obtained dried films. Film thickness was measured with a digital micrometer (IP65, SAMA Tools, Viareggio, Lucca, Italy) at 10 different randomly chosen points.

ASTM D882 (D20 Committee, n.d.-b) method was followed to determine mechanical properties of the materials, using dynamometer (Zwick/Roell, Ulm, Germany). Films were cut into rectangular strips (9 × 1.5 cm^2), the initial grip separation was 70 mm and crosshead speed was 50 mm/min. The results were expressed by software TestXpert®II (V3.31) and were presented as mean value±standard deviation (Etxabide et al., 2024)

2.3.4. Water content (WC) and water solubility (WS)

The method to determine the water content and water solubility followed as it describes by Gontard et al. (1992). The water content (WC) and water solubility (WS) of the films were regulated by gravimetric methods. 1 × 1 cm^2 of the films were weighted (Wi) and the films were dried at 105 °C for 24 h. The dried films were measured (Wf). Eq. (1) was used to measure the WC:

$$WC\ (\%) = \frac{Wi - Wf}{Wi} \times 100 \quad (1)$$

WS was calculated after immersing the dried films into 20 mL of distilled water under rotation (100 rpm). Then, the films were filtered and the undissolved part of the films dried in oven at 105 °C for 24 h. After drying, the films were weighted (Wb). Eq. (2) was used to measure the WS:

$$WS\ (\%) = \frac{Wf - Wb}{Wf} \times\ 100. \tag{2}$$

2.3.5. Surface hydrophobicity

Surface hydrophobicity was determined through measurements of contact angle, according to ASTM D5946 method (D20 Committee, n.d.-a) and sessile drop. Theta Flow Optical Tensiometer (Biolin Scientific, Gothenburg, Sweden) was used to measure the contact angle. Before the analysis, films were stored in a desiccator for at least one week to obtained dried films. A single drop of 4 μL of deionized water were dropped on the surface of the films at ambient temperature (Reuther et al., 2024). The measurement was carried out on 12 random points of each film

2.3.6. Water barrier properties

Water Vapor Transmission Rate (WVTR) and Water Vapor Permeability (WVP) were calculated to determine water barrier properties of the produced films. ASTM E96 method with slight modifications was followed (C16 Committee, n.d.). Glass vials containing 2 g anhydrous $CaCl_2$ (0 % RH) were sealed with the films and placed into a desiccator with $BaCl_2$ (90 % RH). The desiccator was isothermally stored at 40 °C (Etxabide et al., 2024). The following equations were used to calculate WVTR (3) and WVP (4):

$$\mathrm{WVTR} = (\Delta \mathrm{W}/\Delta \mathrm{t}) \times \mathrm{A} \tag{3}$$

$$\mathrm{WVP} = \mathrm{WVTR} \times (\mathrm{L}/\Delta \mathrm{P}) \tag{4}$$

where Δ_W/Δ_t is the weight of vials as a ratio of time (g/day), A (m^2) is the surface area of exposing film, L (mm) is the film thickness and Δ_P is the difference of the vapor pressure between the two sides of the film (kPa). The vapor pressure at 40 °C and RH 90 % is 2.887 kPa.

2.3.7. Optical properties (color & UV-visible barrier)

The color parameters of films were measured according to the CIELAB system with a colorimeter (Eye-one Pro, X-Rite, Michigan, USA). The parameters that were measured were L* (lightness), a* (greenness/redness) and b* (yellowness/blueness). The whiteness index and the total color variation (ΔE*) were calculated using Eq. (5) and (6):

$$\text{Whiteness index (WI)} = 100 - -\left((100 - \mathrm{L})^2 + \mathrm{a}^2 + \mathrm{b}^2\right)^{0.5} \tag{5}$$

$$\Delta E = \sqrt{(\Delta \mathrm{L})^2 + (\Delta \mathrm{a})^2 + (\Delta \mathrm{b})^2} \tag{6}$$

where Δ_L, Δ_a and Δ_b represent the differences between the corresponding color parameter of the sample and the values of a white standard. The measurement was carried out on 10 random points of each film (Etxabide et al., 2024). The results were presented as mean value ±standard deviation.

Spectrophotometer (VWP × Double Beam UV × Vis 6300 PC spectrophotometer, China) was used to measure UV-visible barrier properties. The equipment was set at 190–800 nm wavelength range. The films were cut at $3 \times 3\ cm^2$ and were placed on a paper frame. The opacity of the films was calculated according to the Eq. (7):

$$\mathrm{Opacity} = \mathrm{A}_{600}/\mathrm{x} \tag{7}$$

where A_{600} is the absorbance at 600 nm and x is the average thickness (mm) of the films (Nandi & Guha, 2018).

2.4. Evaluation of the produced films for their applicability in seabream fresh fillets (*Sparus aurata*)

The produced films (HPMC-glycerol, HPMC-linoleic acid, HPMC-oleic acid) were tested for their applicability as packaging material of fresh gilthead seabream (*Sparus aurata*) fillets. Fish fillets were cut into small pieces (10±1 g) and placed into conventional rigid polyethylene terephthalate (PET) containers, which were sealed on the top with the developed HPMC-based materials and polyvinyl alcohol chloride (PVC) as a control, to compare the results with a petroleum based material. The experiment was carried out in cold room storage conditions (2 °C) to simulate flexible covers of the PET trays carrying fresh gilthead seabream fillets in the market.

Microbiological analyses were conducted in order to determine the shelf life of packed fish. 10 g of each sample was collected from PET container and added into a sterile stomacher bag with 90 mL sterilized Ringer solution (Merck, Darmstadt, Germany) and homogenized for 90 s with a Stomacher (BagMixer®, Interscience, Saint-Nom-la-Breteche, France). Zero point one milliliters of tenfold serial dilutions of fish homogenates were spread on the surface of appropriate media in Petri dishes for microbial enumeration. Total aerobic viable count (TVC) was enumerated on Plate Count Agar (PCA; Neogen, Lansing, MI, USA) after incubation at 25 °C for 72 h. *Pseudomonas* spp. were enumerated on Cetrimide Agar (CFC; Condalab, Torrejon De Ardoz, Spain) after incubation at 25 °C for 48 h. For each sample, three dilutions per sampling time were enumerated. Microbial growth was modelled using Baranyi growth model (Baranyi & Roberts, 1995). For curve fitting the program DMFit (IFR, Institute of Food Research, Reading, UK) was used (available at http://www.combase.cc/index.php/en/).

2.5. Statistical analysis

Statical analysis was conducted by one-way analysis of variance (ANOVA) followed by Tukey's multiple range test ($p < 0.05$) with SPSS statical program (SPSS 20 for Windows, SPSS INC., IBM, New York). The results were expressed as mean ± standard deviation (SD).

3. Results and discussion

3.1. Surface morphology

The surface morphology of HPMC films with different plasticizers are presented in Fig 3. SEM allows to study the film microstructure and arrangement of different components in the dried film which are influenced by the evolution during drying. During drying, the solvent evaporation caused changes in the component concentrations and viscosity on the liquid phase ending in variations in the lipid aggregates and creaming phenomenon (Jiménez et al., 2010). The final physicochemical, optical and mechanical properties are influenced by the interactions between the film components which determine the morphological structure of the films (Bigi et al., 2021). The surface of HPMC films with glycerol as a plasticizer was smooth as well as it had a homogeneous and uniform matrix with small particles, indicating the formation of an ordered matrix and the well distribution of glycerol into the polymer matrix. Lower compatibility between HPMC and linoleic acid was observed as Fig 3c shows surface with pores and bubbles. This may be attributed to the different nature of the components as HPMC is a hydrophilic (water soluble) material (Deshmukh et al., 2017) while linoleic acid is a hydrophobic compound (Rodrigues Freitas et al., 2016). The surface morphology of the sample added with oleic acid was similar to the one with linoleic acid, but with less bubble, indicating a better compatibility with aqueous solvents. Oleic acid is a monosaturated fatty acid which has one double *cis* bond while linoleic acid is polysaturated fatty acid which has double *cis* bonds. As the results when the fatty acids diffused in HPMC film forming solution oleic acid had less bonds to break required less energy and time to interact with the polymer and form bonds leading to the better dispersion (Lichtenstein, 2023; Vu et al., 2022). Similar results were obtained with the addition of oleic acid to sodium caseinate films as films containing oleic acid are not laminar in structure due to the absence of bilayer self-association of the molecules. Oleic acid has a fine distribution and lipid droplets are homogeneously dispersed in biopolymer matrix (Fabra et al., 2009). The increase of oleic acid content in the films modifies significantly surface topography releasing a different amount of lipid particles on the surface.

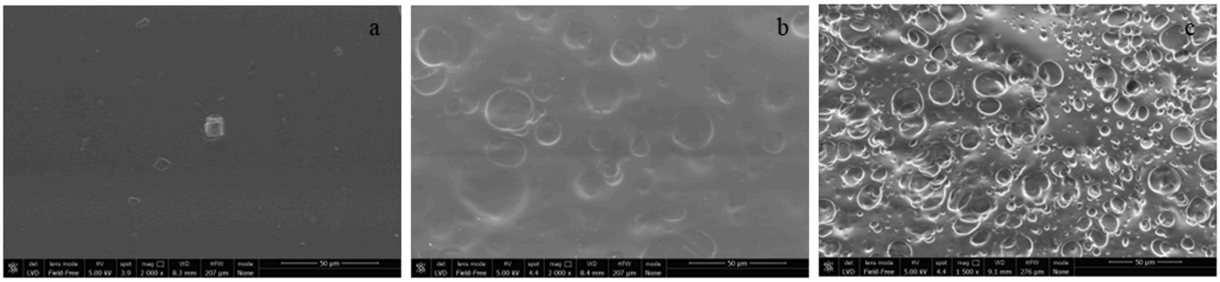

Fig. 3. SEM images of films based on HMPC with (a) glycerol, (b) oleic acid, and (c) linoleic acid.

It is proven that a great ratio of droplet can be observed in the upper part of the films rather than in the bottom part, which validates the phenomenon of creaming during the film drying (Vargas et al., 2009). Jiménez et al. (2010) studied the effects of different fatty acids in HPMC matrix and pointed out the lipid layer was formed in the film with the use of lauric, myristic, palmitic acid while the use of stearic or oleic acid into HPMC matrix primarily formed a non-layered structure and the lipids distributed perfectly. These two lipids had very small particles in the film forming emulsion resulting in lower viscosity compared to the HPMC solution. This suggests that specific interactions between the polymer and lipid are likely to take place preventing the micelles from growing, both in the initial film-forming emulsions and during their drying process.

HPMC films mixed with acids have a smoother surface compared to pure HPMC films, which indicates a good integration of acids into the HPMC matrix, leading to a very homogenous, tighter structure. However, in other cases, such as ginger oil droplets, the structure of films exhibits discontinuities correlated with oil droplets. Films mixed with oil may be thicker than other films which can be assigned to that the polymer chain aggregation is made difficult by the presence of oil droplets and the film has an open structure (Atarés et al., 2011).

3.2. Fourier-transform infrared (FT-IR) spectroscopy

HPMC films containing different plasticizers (glycerol, oleic acid and linoleic acid) were selected for FTIR analysis to find out any chemical interaction between HPMC and plasticizers. ATR/FTIR spectroscopy was used as a non-destructive and rapid technique to give us information on the different chemical functionalities of HPMC with different plasticizers. Structural changes and intermolecular interactions of the polymers and plasticizers are interpretated by spectroscopic changes (Haghighi et al., 2019). The IR spectrum of HPMC with glycerol as plasticizer (Fig 4) showed characteristics peaks at 3311 cm^{-1} that can be associated with the hydroxyl groups and a very strong absorption band at 1035 cm^{-1} assigned to the ν_{as}(C—O-C) of pyranose ring skeletal vibrations (Akhtar et al., 2012). The stretching vibrations of methyl, propyl, and CH groups of HPMC are represented by the band complex between 3000 and 2800 cm^{-1}. The band at 1647 cm^{-1} can be associated with bound water (Hay et al., 2018).

Spectra of fatty acid have peaks at 1100, 1670–1710, and 2850–2960 cm^{-1} represent the C—O-C, -OH, C—H and $C = O$, respectively (Hassabo, 2018). Spectra of prepared materials showed peaks between 3500–2500 cm^{-1} region are due to O—H stretching of carboxylic acid groups (-COOH) that are presented in oleic and linoleic acid structures. Two sharp peaks appeared at 2854 and 2920 cm^{-1} for oleic and 2918 and 2856 cm^{-1} for linoleic acid are associated with O—H symmetric and asymmetric -CH$_2$ stretching vibrations, respectively. The sharp peaks showed at 1706 cm^{-1} (for films with oleic acid) and 1722 cm^{-1} (for films with linoleic acid) reflects mainly due to $C = O$ stretching (Premaratne et al., 2014). The peak of 1060 cm^{-1} for films with oleic acid as plasticizer with high transmittance shows the -COOH bond of the carboxyl group (Vu et al., 2022) and the peak of 933 cm^{-1} responds to O—H stretch out-of-plane (Hafızosmanoğlu et al., 2024). FTIR spectrometry measurements showed that fatty acid molecules migrate on the surface of the synthesized films, the driving force being the microphase separation between the polar HPMC macromolecules and the hydrophobic nature of fatty acids, resulting in the formation of a weak boundary layer with poor cohesion. Brogly et al. (2024) tested the incorporation of

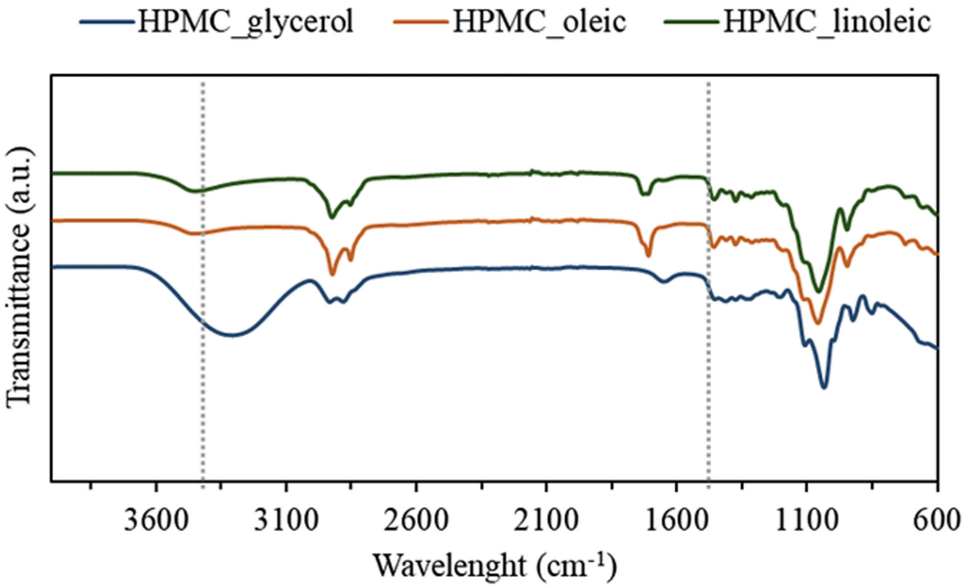

Fig. 4. The FTIR profiles of HPMC based films with different plasticizers.

stearic acid in hypromellose matrix indicating the accumulation of fatty acid on the film's surface is shown by the increase in IR band intensity observed with stearic acid content in hypromellose films in region of CH_2 stretching modes.

Ursachi et al. (2024) produced films from 2 % HPMC and glycerol as plasticizer in ratio of HPMC_glycerol 0.9:0.1 (w/w) and they tested FT-IR spectrum. They pointed to an absorptive peak at 1642 cm^{-1} representing the presence of $C = O$ stretching of carbonyl group. Other studies show C—H stretching vibrations at 2920 and 2852 cm^{-1} in the spectrum of oleic acid and carbonyl stretching vibration at 1710 cm^{-1} (Baek et al., 2018; Hafızosmanoğlu et al., 2024).

3.3. Thickness and mechanical properties

According to Table 1, HPMC films with glycerol were thinner compared to the films with hydrophobic plasticizers. This may be attributed to the fact that glycerol was well dispersed, and the produced films were more compact.

Tensile strength, elongation at break, and young's modulus are the three more important parameters to study when examining biodegradable films for their mechanical properties. The nature of the polymer, the preparation method and the composition of the film are the factors that affect the mechanical properties. The mechanical properties influence other parameters of film such as crystallinity, barrier properties, and thermal stability (Shah et al., 2023). The films with linoleic acid as plasticizer had lower tensile strength and young's modulus indicating that these films had less maximum strength that can endure before breaking, making more flexible films but weaker as they cannot stand high forces without break (Kong et al., 2022). The less compact matrix for films with high number of bubbles may be responsible for lower values of tensile strength and young's modulus in HPMC_linoleic acid films (9.04±2.41 MPa and 387.69±95.70 MPa, respectively). Glycerol plasticized films showed the higher values of tensile strength and young's modulus. Among the films higher values of elongation at break were the oleic acid plasticized films (30.35±4.21 %). Natural based polymers show low ductility because of the strong hydrogen bonding between their integral molecules, ending in a stiff structure (Mukherjee et al., 2024). For edible films, a high elongation is acceptable since it increases the film's capability to wrap food. After plasticization with oleic acid the tensile strength and young's modulus decreased and elongation at break increased, compared to glycerol plasticized films. These changes make materials more suitable for use as malleable inner packaging (Zhang et al., 2018). The oleic acid formed lipid aggregates in the film, which prevented premature breakage during deformation in the mechanical tests. This effect result in a better dispersion of oleic acid compared to linoleic acid, as it is shown from SEM images, and a better plasticizer effect on the selected polymer (Jiménez et al., 2010). Films with oleic and linoleic acid tended to be weaker and exhibited lower tensile strength compared to films plasticized with glycerol, which could be associated with discontinuous areas in the film structure, as it is described in Section 3.1. The addition of linoleic acid resulted in greater extensibility, which may be attributed to the deterioration of the polymer chain aggregation connected with oil presence and the liquid state of linoleic acid at room temperature and the elongation of oil droplets as the structure is stretched (Atarés et al., 2011). According to the study of Fabra et al. (2009) oleic acid, compared to glycerol plasticized films, improved the flexibility and deformability of sodium caseinate films coherently with the liquid state of the lipid, while lauric, stearic, and palmitic acid which are saturated fatty acids and solid at room temperature, significantly increased the tensile strength and young's modulus and reduced the elongation at break which restricts the deformation of the dispersed phase of the sodium caseinate films when being stretched.

Table 1
Thickness (μm), tensile strength (MPa), youngś modulus (MPa) and elongation at break (%) of HPMC based films.

Film	Thickness (μm)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
Glycerol	45.43 ±3.33^{a}	26.02±3.05^{c}	1613.22 ±492.88^{c}	7.98±0.96^{a}
Oleic acid	73.00 ±3.43^{b}	18.47±3.64^{b}	518.21 ±50.10^{b}	30.35±4.21^{b}
Linoleic acid	71.13 ±2.45^{b}	9.04±2.41^{a}	387.69 ±95.70^{a}	8.87±2.33^{a}

$^{a-c}$ Different superscripts in the same column indicate statistically significant differences.

Imran et al. (2010) produced films with HPMC and different concentrations of glycerol, obtaining similar results for tensile strength. In particular, at the concentration of 20 % w/w of glycerol, they obtained a tensile strength of 21±2 MPa, a young's modulus of 961±92 MPa, and an elongation at break of 41±13 %. Akhtar and Aïder (2018) prepared bioactive edible films with HPMC, non-electro-activated whey and electro-activated whey. They used glycerol as plasticizer, and they tested two concentrations (1 % and 4 % w/v). The authors pointed out that glycerol resulted in more flexible, weaker and stretchable films and by increasing the glycerol concentration the tensile strength and young's modulus were decreased, while elongation at break increased significantly.

3.4. Water content (WC) and water solubility (WS)

The water content (%), and the water solubility (%) are presented in Table 2. Depending on the industrial applications of HPMC films the high solubility may be acceptable or not. Some applications demand the insolubility of packaging materials to confirm the integrity and strength of the food which is being packed. In other applications, the film solubility is acceptable to release active compounds, such as antimicrobials and antioxidants (Rotta et al., 2009). The percentage of water content and water solubility was high in case of HPMC_glyecrol films (77.26 ±2.75 % and 69.18±0.80 %). Films with glycerol have high water content because glycerol acts as a humectant and absorbs water molecules from the surrounding environment. When glycerol is added to cellulose films, it interacts with water molecules through hydrogen bonding. Additionally, glycerol can disrupt the crystalline structure of the cellulose, increasing the free volume and creating more binding sites for water (Khotsaeng et al., 2023).

When fatty acids were used as plasticizers the WC and WS percentages were significantly lower. Although the water content of HPMC_linoleic acid films was the lowest (8.49±1.76 %), the lowest water solubility values were represented by HPMC_oleic acid films (19.03 ±0.98 %). Rosenbloom and Zhao (2021) produced films from HPMC and 0.1 % or 0.2 % DL-α-tocopherol acetate and 0 or 0.25 % oleic acid were added into the matrix as antioxidant and hydrophobic compound, respectively. The results indicated that in water at 20 °C and 40 °C all films decomposed faster than 15 s and completely dissolved at 1–4.5 min. The films with 0.1 % DL-α-tocopherol and 0.25 % oleic acid were the most cohesive. The authors correlated this trend with the WVP analysis in which the film with 0.1 % DL-α-tocopherol and 0.25 % oleic acid had the lowest permeability.

Vlacha et al. (2016) pointed that the use of plasticizer led to a

Table 2
Water content (%), water solubility (%) and contact angle (°) of HPMC based films.

HPMC based film	Water content (%)	Water solubility (%)	Contact angle (°)
Glycerol	77.26±2.75^{c}	69.18±0.80^{c}	81.47±6.65^{a}
Oleic acid	13.42±1.91^{b}	19.03±0.98^{a}	94.71±9.63^{b}
Linoleic acid	8.49±1.76^{a}	41.08±1.00^{b}	99.48±2.32^{b}

$^{a-c}$ Different superscripts in the same column indicate statistically significant.

significant reduction of weight gain of chitosan based films plasticized with glycerol or oleic acid when the films were sub-immersed in water, resulting in extensive formation of hydrogen bonds, swelling of the films and partial dissolution of chitosan. The reduction of weight gain was higher at higher concentrations of plasticizers while the addition of glycerol was more beneficial compared to the use of oleic acid. This phenomenon can be linked with the reduction of the free volume in case of glycerol plasticized films due to the better packing of the polymer chains. The authors concluded that films with glycerol presented higher diffusion coefficient compared to those with oleic acid. The use of plasticizer led to lower water sorption ability of films as the carboxylate groups of oleic acid and the hydroxyl groups of glycerol can interact with the functional groups of the polymer, forming a matrix which does not permit water to further interact with the polar groups of the polymer.

3.5. Surface hydrophobicity

The hydrophobicity of the film surface was determined by measuring the contact angle of the film. When the contact angle is higher than 90° the film is characterized as hydrophobic, while the surface of the film corresponds to hydrophilic when the contact angle is equal or lower than 90° (Xu et al., 2019). The contact angles of the plasticized films are presented in Fig 5 and their values are shown in Table 3. The surface films plasticized with fatty acids were hydrophobic. The contact angle was 94.71±9.63° for films with oleic acid and 99.48±2.32° for films with linoleic acid. There were no statistically significant differences between the two types of fatty acids. This may be attributed to the hydrophobic backbone of fatty acids chain Kohlmeier (2015). Glycerol has three hydroxyl groups and is recognized for its hydrophilic nature, leading to production of hydrophilic films (the contact angle of HPMC_glycerol film was 81.47±6.65°).

Hydrophobicity is a valuable characteristic in the food packaging materials because it assists repel water and liquids contributing to extent the shelf life of food products (Asim et al., 2022). The decrease of -OH groups enhance the hydrophobicity of the materials. Kallakas et al. (2023) produced cellulose fatty acid ester films indicating that by increasing the length of fatty chain, the contact angle increased. Films with acetate (C12) had a contact angle equal to 84.94±0.23° while films with stearate (C18) had contact angle equal to 104.01±4.04° Angles higher than 90° were observed in films with C16 and C18 fatty acids. There are several studies which show that the increase in chain length and degree of substitution produce more hydrophobic cellulose esters (Crépy et al., 2009; Lease et al., 2023; Sejati et al., 2023; Shorey & Mekonnen, 2024; Wen et al., 2017).

The change of hydrophilic degree of hydrocolloids coincides with how chitosan-based films plasticized with oleic acid behaved when the acid content increased, as observed by Vargas et al. (2009). This is referable to the fewer sites available for water sorption in the polymeric matrix because of the higher concentration of hydrophobic chains from the fatty acid. The molecules of polymer are becoming less hydrophilic because of the electrostatic neutralization of HPMC hydroxyl groups with the carboxylate groups of oleic acid. This implies that, as the film becomes more hydrophobic, the water molecules are absorbed with less energy in the active sites (Vargas et al., 2009).

Table 3
Water Barriers (water vapor transmission rate, WVTR and water vapor permeability, WVP) of HPMC based films.

HPMC based film	WVTR (g/day × m^2)	WVP (g × mm/day × m^2 × Pa)
Glycerol	1999.24±75.30[c]	32.33±2.25[c]
Oleic acid	767.52±55.70[b]	21.64±1.79[b]
Linoleic acid	355.94±29.53[a]	7.67±1.29[a]

[a-c] Different superscripts in the same column indicate statistically significant.

3.6. Water barrier properties

Water barrier properties are crucial in food packaging systems to avoid transfer of moisture between the environment and the food. Moisture barriers are evaluated through WVP and WVTR and lower values are preferred since it can reduce the moisture loss of enveloped food products, for example for fruits and vegetables (Li et al., 2022). Table 3 presents the values of WVTR (g/day × m^2) and WVP (g × mm/day × m^2 × Pa) of produced films. The glycerol plasticized films had statistically significantly higher values of water barrier compared to films with fatty acids as plasticizers. The high WVP of HPMC_glycerol films are due to the high number of hydrophilic groups such as -OH, and -COOH in the polymer molecule chains and in the plasticizer structure as well (Long et al., 2023). Except for the number of hydroxyl groups, the water affinity also influences the WVP values. Glycerol shows high water affinity due to its low molecular weight (92 Da) providing higher molar content for glycerol-plasticized film (Malik et al., 2022). Significant increase of WVP with glycerol addition has been previously reported (Espinel Villacrés et al., 2014; Ghadermazi et al., 2019; Laboulfie et al., 2013; Malik et al., 2022) because glycerol is a relatively small hydrophilic molecule, which can be added into the adjacent polymeric chains, diminishing intermolecular attractions, hence, the migration of water vapor molecules makes easier (Vlacha et al., 2016). When oleic acid was used as a plasticizer the WVTR and WVP decreased statistically significantly (767.52±55.70 g/day × m and 21.64±1.79 g × mm/day × m^2 × Pa, respectively). The use of linoleic acid led to a further decrease in permeability and transmission of moisture values. The difference in WVTR and WVP when incorporated linoleic or oleic acid in cellulose films may be due to the molecular structure of these fatty acids. Linoleic acid has two double bounds and thus creates more rigid packaging in the film, reducing the free volume and finally the water vapor permeability. Oleic acid, has only one double bond, making less rigid packing films which leading to higher permeability (Lichtenstein, 2023; J. J. Wang et al., 2024). Another possible explanation is that linoleic and oleic acids

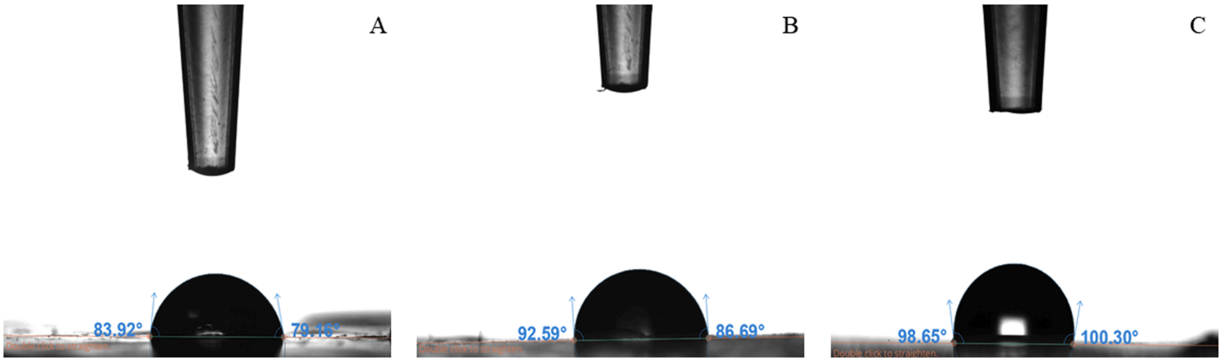

Fig. 5. Water drops on the surface of HPMC based films with (A) glycerol, (B) oleic acid, and (C) linoleic acid as plasticizers.

have a considerably longer chain (C18) than glycerol (C3) resulting in the formation of a continuous lipid phase which has been connected with higher efficiency as barrier to WVP (Aguirre-Loredo et al., 2014). However, both oleic and linoleic acid are low polarity substances and they can restrict the permeation process when their ratio in the polymeric matrix reaches a critical level, by reducing the number of polar groups available to interact with water molecules (Villalobos et al., 2006). A similar reduction to WVP was also observed by Mukherjee et al. (2024) by the incorporation of cetylcaprylate and cetylcaprate esters in carboxymethyl- cellulose matrix.

Budi Santosa and Padua (1999) compared the water resistance of plasticized zein films with oleic and linoleic acid and they concluded that linoleic acid was more effective than oleic acid at minimizing water absorption of films. They attributed this phenomenon to linoleic acid polymerization, which may have filled pores and gaps in the structure blocking it from swelling. Fakhouri et al. (2009) synthesized composed layer films by lipophilic starch, gelatin and sorbitol containing different amounts of fatty acids (palmitic, lauric, myristic, capric, caproic and caprylic), at concentrations 5, 15, 25 and 50 %. The addition of fatty acids reduced the WVP to concentrations up to 25 %. The authors suggested that for all the fatty acids tested, concentrations higher than 25 % increased the WVP values because the maximum amount of lipids that allowed the synthesis of a homogenous gellan film was 25 % based on the dry mass of the polymer. Higher concentrations of lipids are not homogeneously distributed, due to their low dispersion and to the poor stability of the emulsion system at the higher concentrations. Similar results for the high values of WVP of glycerol plasticized biobased films have been reported by other authors with different polymer matrix (Ballesteros-Mártinez et al., 2020; Farhan & Hani, 2017; Gheribi et al., 2018).

3.7. Optical properties (color & UV-visible barrier)

The optical properties (color parameters, opacity, transparency, and light transmission) are imporant and influential parameters for consumer satisfaction and acceptance. The color of the films is influenced by different factors such as film thickness and density (Pirsa & Mohammadi, 2021).

As it is presented in Table 4 HPMC based films with glycerol as plasticizers had the lowest values of L* which represents the lightness and WI, while the color difference (ΔE) between the films and white standard was the highest (1.36±0.10). ΔE values between 1 and 2 indicates a difference in the color of two tested materials that can be perceived by close observation (Brainard, 2003). Ureña et al. (2023) underlined that glycerol concentration affects the color of films over time as when they used 20 % glycerol in produced films the ΔE* was two times higher than that of films without glycerol.

For films with oleic and linoleic acids as plasticizers ΔE was lower than 1 evidencing that the differences between the films and white standard are not detectable with naked eye. Vargas et al. (2009) investigated the use of oleic acid in chitosan matrix and reported that the addition of oleic acid enables a significant increase in the whiteness index of the chitosan_oleic acid films compared to pure chitosan films. The light selective absorption of oleic acid at low wave lengths transmits the yellowness to the films.

Table 4
CIELab (L*, a*, b*) parameters, color differences (ΔE), whiteness index (WI) and opacity values of HPMC based films.

HPMC based film	L*	a*	b*	ΔE	WI	Opacity
Glycerol	97.98 ±0.41^{a}	−0.15 ±0.02^{c}	0.41 ±0.01^{b}	1.36 ±0.10^{c}	97.84 ±0.41^{a}	0.0023 ±0.0003^{a}
Oleic acid	99.29 ±0.03^{b}	−0.45 ±0.02^{a}	0.46 ±0.01^{c}	0.67 ±0.07^{b}	98.92 ±0.19^{b}	0.0128 ±0.0001^{c}
Linoleic acid	99.34 ±0.10^{c}	−0.29 ±0.01^{b}	−0.32 ±0.04^{a}	0.33 ±0.03^{a}	99.21 ±0.07^{c}	0.0081 ±0.0016^{b}

[a-c] Different superscripts in the same column indicate statistically significant.

As shown in Fig 6 the films with glycerol as plasticizer were more transparent (the line behind the film is clear while the lines behind the films with oleic and linoleic acid as plasticizers are not visible). This fact is also confirmed by the lowest opacity value. In general, all produced films had very low opacity values, and as results the films were transparent and clear (Table 4). The internal structure formed during drying process affects the transparency level. For example, volume fraction of the dispersed phase and size of polymer-fatty acids aggregates are changed at this step of the film synthesis. During drying, the solvent properties of the continuous phase change, resulting in coalescence and creaming phenomena as water is reduced. Simultaneously, the viscosity of the continuous phase increases, restricting the aggregation and creaming, which leading to a specific dispersion level of lipid components (such as oleic and linoleic acid) in the polymer matrix and a certain degree of anisotropy in the physical properties throughout the matrix (Villalobos et al., 2005). Brogly et al. (2024) prepared films from HPMC and stearic acid at 0 %, 0.1 % and 1 % and they pointed that pure HPMC was clear, transparent, homogenous and uniform while the increasing content of stearic acid led to increase the glossy properties and the whiteness of the films. The authors concluded that similar results in the opacity of the films as the lipid incorporation leads to an increase in film opacity. The phenomenon may be attributed to light scattering from lipid droplets dispersed into the film network after its formation.

In UV region (210 nm), the HPMC films with glycerol had the higher rate of transmittance (80.99±0.02 %) compared with films with fatty acids (11.88±0.01 % and 23.89±0.05 % for films with oleic and linoleic acid, respectively). In the visible region (500 nm) the transmittance of HPMC films was 76.07±0.02 %, 11.16±0.01 % and 23.20±0.05 % for films with glycerol, oleic acid and linoleic acid, respectively (Fig 7). Comparing the transmittance of UV region with visible region we noted that the rate of transmittance was lower at 210 nm in the case of films with glycerol indicating that films had goof preventive ability against radiation UV.

Rotta et al. (2009) produced films from HPMC and compared them with films from chitosan and with composite films HPMC_chitosan. They used 10 % sorbitol as plasticizer. They pointed out at 210 nm the HPMC films had a high rate of transmittance (63.7 ± 1.83 %), compared with chitosan films (4.63±3.55 %) and blends of HPMC_chitosan. In the visible region (500 nm), the transmittance of HPMC films was high (93.76 % ± 2.02), and they concluded that HPMC films had a good preventive ability against radiation UV.

3.8. Microbiological evaluation of packed gilthead seabream fillets

The effect of HPMC films with different plasticizers was studied in terms of microbial growth of the fish fillets at isothermal conditions at 2 °C and the results are presented in Fig 8. The initial natural microbiota of unpacked fish fillets was equal to 4.07±0.26 and 3.92±0.63 logCFU/g for TVC and *Pseudomonas* spp., respectively. The results showed that the populations of all tested conditions increased as a function of storage time. The initial TVC is in agreement with reported initial microbial load od seabream fillets and other mediterranean species (Koutsoumanis et al., 2002; Papaharisis et al., 2019; Spanou et al., 2024). Basdeki et al. (2023) pointed out that different spoilage rates are influenced by differences in the initial populations of surface bacteria.

No significant differences were observed in microbial growth rates between the different tested plasticized films. According to Table 5, the final microbial populations ranged between 9.16±0.15 and 10.17±0.96 logCFU/g for TVC and 9.13±0.26 and 10.04±0.15 logCFU/g for *Pseudomonas* spp. According to Alexi et al. (2022) 10^{7} CFU/g for TVC is the limit of acceptability and based on this limit the shelf life of the gilthead seabream was calculated. The results showed that the shelf life of fish

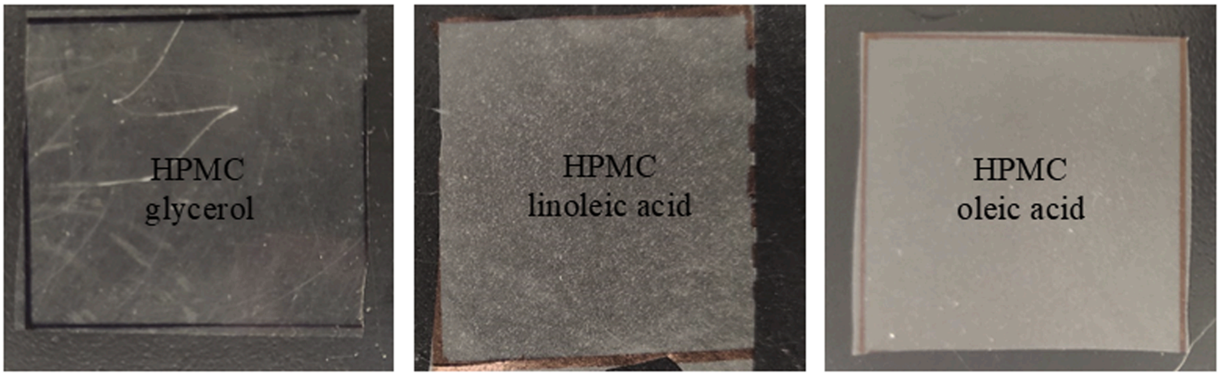

Fig. 6. Optical appearance of HPMC based films with (A) glycerol, (B) oleic acid, and (C) linoleic acid as plasticizers.

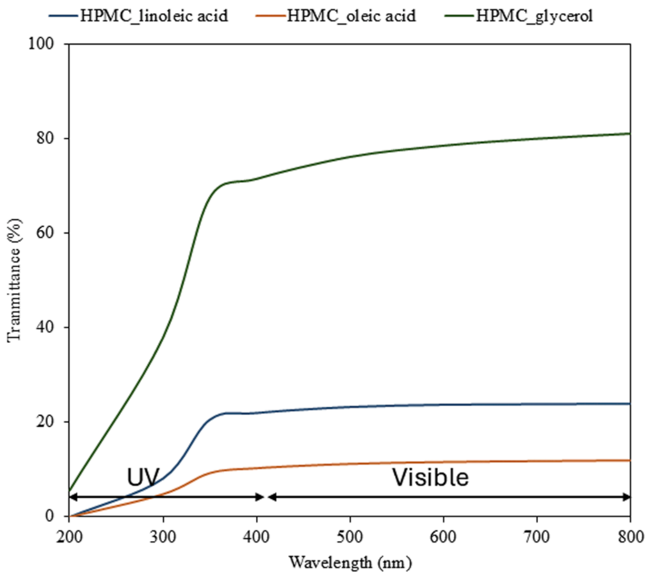

Fig. 7. UV-visible transmission spectra of HPMC based films with glycerol (green line), oleic acid (red line) and linoleic acid (blue line) as plasticizers.

ranged 7–8 days at 2 °C without significant differences between the tested packaging materials which agrees with other studies in the literature evaluation of Mediterranean fish fillets (Athanasopoulou et al., 2024; Muscolino et al., 2016; Tsironi & Taoukis, 2017).

Günlü and Koyun (2013) studied the effect of vacuum packaging and chitosan based edible films in preservation of sea bass. The edible films had glycerol as plasticizer. The temperature of storage was 4 °C and the samples were stored until the end of their shelf life. They found that the initial counts of psychrotropic bacteria were 4.87 logCFU/g and of mesophilic aerobic bacteria were and 5.89 logCFU/g in sea bass filets. They found that the shelf life of samples coated with chitosan and stored at vacuum packaging was 25 days while the shelf life of samples only with chitosan coating or only with vacuum packaging was 5 days. Polysaccharides films or coatings have been used in the literature to reduce or inhibit microbial growth on fish and seafood products (Fan et al., 2009; Gómez-Estaca et al., 2010; Jeon et al., 2002; Ojagh et al., 2010; Rico et al., 2020; Vásconez et al., 2009).

Sun et al. (2025) developed a bilayer active packaging film from soy lipophilic protein and HPMC enhanced with nanoemulsion from thyme essential oil and shikonin as the oil phase and they tested the applicability of the films for the preservation of salmon. They reported that the bilayer film with oil has better results the single layer film because of its unidirectional release which limited microbial growth more effectively and controlled the freshness of the salmon by the discoloration effect.

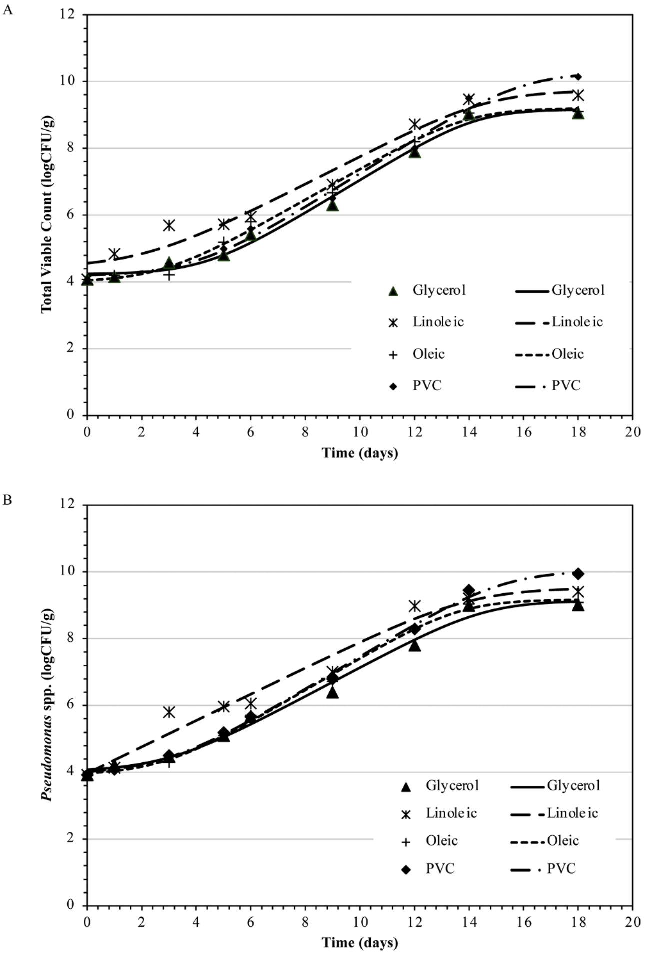

Fig. 8. (A) Total viable count and (B) *Pseudomonas* spp. in seabream fillets packed with HPMC based films with different plasticizers (glycerol, oleic acid and linoleic acid) when stored at 2 °C compared with seabream fillets packed with PVC films. The dots represent the experimental values for microbial enumeration, while the lines illustrate the microbial growth curves obtained from the Baranyi fit.

The results of the present study showed that the HPMC based materials with glycerol, oleic acid or linoleic acid as plasticizers may limit the use of petroleum based polymers such as polyvinyl chloride without affecting the shelf life of the packed fish.

Table 5

Baranyi parameters i.e., k: growth rate (d^{-1}), λ: lag phase (d) and N_{max}: maximum population at the end of storage (logCFU/g) of microbial growth of gilthead seabream fillets packed with HPMC and different plasticizers.

HPMC based film	k (d^{-1})	λ (d)	N_{max} (logCFU/g)	R^2
TVC				
Glycerol	0.50±0.05^{c}	4.35±0.16^{c}	9.16±0.15^{a}	0.99
Oleic acid	0.46±0.03^{b}	2.82 ±0.61^{b}	9.20±0.07^{a}	0.99
Linoleic acid	0.41±0.02^{a}	2.34±0.29^{a}	9.72±0.05^{b}	0.96
PVC	0.51±0.02^{c}	4.05±0.32^{c}	10.27±0.96^{c}	0.99
***Pseudomonas* spp.**				
Glycerol	0.43 ±0.02^{b}	3.00±0.09^{b}	9.13±0.26^{a}	0.98
Oleic acid	0.48±0.01^{c}	2.86±0.17^{b}	9.17±0.54^{a,b}	0.99
Linoleic acid	0.39±0.01^{a}	0^{a}	9.52±0.32^{b}	0.96
PVC	0.49±0.12^{c}	2.99±0.09^{b}	10.04±0.15^{c}	0.99

$^{a-d}$ Different superscripts in the same column indicate statistically significant.

4. Conclusion

Added plasticizers were found to be effective in favorable flexibility in terms of elongation at break to HPMC film which is important for making appropriate films for fish packaging. Glycerol was quite effective as a plasticizer for HPMC films. WVP, water content and water solubility of the produced films were higher as compared to hydrophobic plasticized films. Tensile strength and young's modulus were lower in HPMC_linoleic acid materials which had many bubbles as proved by SEM images. Films plasticized with oleic acid had very good elongation at break and acceptable tensile strength. Overall, the results showed the potential application of biodegradable HPMC-based films as green eco-friendly packaging materials to sufficiently maintain fresh gilthead seabream fillets at refrigerated conditions.

CRediT authorship contribution statement

Evmorfia Athanasopoulou: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Enrico Maurizzi:** Writing – review & editing, Validation, Methodology, Investigation. **Francesco Bigi:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis. **Andrea Quartieri:** Writing – review & editing, Validation, Resources, Methodology. **Andrea Pulvirenti:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization. **Theofania Tsironi:** Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

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

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Data availability

Data will be made available on request.

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