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Solid dispersions as effective curcumin vehicles to obtain k-carrageenan functional films for olive oil preservation

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A B S T R A C T

Synthetic packaging materials offer cost efficiency and performance but pose environmental risks. This study explores sustainable alternatives by developing k-carrageenan (KC) films functionalized with curcumin, using solid dispersions (SDs) to improve curcumin's compatibility, addressing the challenge of incorporating hydrophobic functionalities into hydrophilic film matrices. Films with varying curcumin content (1–20 wt%; KC1-KC20) were compared to a base film without curcumin (KC0) regarding water solubility, vapor permeability, water contact angle, and tensile properties. Compared to KC0, KC10 (10 % curcumin-SDs) exhibited improved water resistance, with solubility decreasing from 82.89 % to 77.18 %, while maintaining vapor permeability (2.96×10^{-10} g·m/s·m^2·Pa). KC10 demonstrated enhanced tensile properties, with a 12.51 % increase in tensile modulus (241.47 MPa), a 3.86 % increase in stress at break (3.50 MPa), and a 4.42 % increase in strain at break (2.36 %). Furthermore, it exhibited potent antioxidant activity without releasing curcumin into a simulated fatty medium (non-migratory active protection mechanism), effectively preserving olive oil by limiting lipid oxidation to a peroxide value (PV) of 14 mEq. O_2/kg oil, compared to 20 mEq. O_2/kg oil in unprotected samples under accelerated conditions. It demonstrated significant antimicrobial activity with bacterial reductions of 95.4 % (*Escherichia coli*) and 90.6 % (*Listeria monocytogenes*), surpassing KC0. In conclusion, k-carrageenan films functionalized with curcumin SDs are promising and sustainable alternatives to synthetic packaging materials.

1. Introduction

Synthetic polymeric materials are widely used in several areas, including packaging applications. In the food area, the primary objective of packaging materials is to safeguard products against contamination and spoilage, facilitating efficient transportation and storage while ensuring final safety and quality [1,2]. With the growing environmental awareness, the interest in using natural-based materials in packaging solutions is rising. This shift presents an opportunity to address sustainability concerns, reduce reliance on non-renewable resources, and mitigate the environmental impact of traditional packaging materials [3,4].

Significant and widespread focus has been directed to developing intelligent and active packaging materials to meet market demands. In this context, polymeric materials can be engineered with specific barrier properties to limit the transfer of oxygen, moisture, and other gases across the package, with oxygen control being critical for many spoilage reactions, such as oxidative rancidity, which result in off-flavors and a decline in quality, especially in products such as olive oil. Active compounds can also be incorporated into materials to provide antioxidant and/or antimicrobial activity, enhancing the material's functional effectiveness [5].

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Polysaccharides' strong hydrogen bonding ability offers several advantages for packaging applications. Among them are functionality and stability enhancement due to the facilitated linkage to functional additives (e.g., colorants, flavors, and active compounds). Moreover, they can act as barriers to oxygen permeation [6], which is the case of K-carrageenan (KC). KC, a polysaccharide derived from red seaweed and composed of galactose and 3,6-anhydrogalactose units, can form gels, with its double helix structure contributing to achieving stable networks. These attributes facilitate the development of films and coatings, especially when combined with compounds enhancing their final properties. Examples include the addition of KC films with SiO_2 and silver nanoparticles [7,8] and bioactive compounds (e.g., essential oils and derivatives, extracts of germinated fenugreek seeds, honey, and bee pollen) [9–12].

Carotenoids have been investigated in the packaging area, with curcumin receiving considerable attention for its numerous beneficial properties, such as antioxidant and antimicrobial activities [4,13]. Furthermore, the changes in color and structure caused by pH variations were explored as indicators of food spoilage for packed fresh meat and fish (beef, chicken breast, pork, and silver carp) [14–17]. The incorporation of curcumin into KC-based films has been explored only in a few studies [18,19]. Some examples include films using mixtures of KC with gelatin to preserve grass carp fillets [20] and KC with gelatin and zein for permeable films to detect raw Atlantic salmon and oyster freshness [21]. Since curcumin is a lipophilic compound, an intermediate step of dissolution in ethanol was needed to enable its addition into the hydrophilic polymeric matrix.

Besides the challenge of compatibility between curcumin and the hydrophilic polymeric matrix, incorporating curcumin in its raw form can lead to its deterioration, as it is highly susceptible to light, heat, and oxygen degradation. In this context, pre-treatments have been employed, with encapsulation techniques used to facilitate the incorporation of curcumin and maximize its effects [22,23]. In recent studies, curcumin-β-cyclodextrin inclusion complexes were developed to improve curcumin water solubility and stability and then tested as photodynamic antibacterial films [24,25]. Another example involves synthesizing nanoparticles using a layer-by-layer technique where curcumin-zein particles were coated with epigallocatechin gallate (a polyphenolic compound from green tea) and lambda-carrageenan, for incorporation into lambda-carrageenan films [26].

Solid dispersions (SDs) are a promising method for enhancing the water solubility of hydrophobic compounds like curcumin. This technology involves dispersing a typically hydrophobic and crystalline active compound within a solid matrix, often a hydrophilic polymer, promoting amorphization and improving water solubility [27,28]. Additionally, SDs enhance the stability of curcumin against environmental factors, as reported in a previous work where the effect of pH and cooking temperatures was evaluated [29], suggesting that similar effects can be expected in the functionalized films.

The incorporation SDs in films has been investigated in a limited number of studies. Examples include gastro-retentive expandable films made from starch/chitosan incorporating ginger extract-loaded polyvinylpyrrolidone SDs [30] and curcumin-loaded Eudragit EPO SDs [31]. These systems were designed to improve therapeutic efficacy for gastric diseases, showing notable enhancements in solubility and sustained release, highlighting the potential of SD-based films for targeted gastric treatments. Concerning food packaging, poly(ε-caprolactone) films containing sage extract SDs were produced through electrospinning [32], and starch films were reinforced with curcumin solid dispersions (SDs) formulated using steviol glycoside [33].

In this study, KC films functionalized with curcumin using KC-based SDs were produced and tested as packaging materials for olive oil preservation. The advantages of this strategy were inspected by producing films with different curcumin-SD contents (0–20 % wt%), followed by extensive characterization. Firstly, properties like thickness, color, optical transparency, water solubility, water vapor permeability, water contact angle, and tensile properties were determined. The best formulations were subjected to morphological analysis, release studies in simulated food media, and antioxidant activity evaluation, followed by olive oil preservation studies. This was evaluated by measuring the peroxide index under accelerated conditions. Moreover, in the final step, the antibacterial activity of the most promising film was accessed to extend its potential applications. To the best of our knowledge, this is the first study to explore KC-curcumin SDs for functionalizing films made from the same polymeric material. This method allows curcumin integration in a water-compatible form (SDs) within the KC film, promoting uniform distribution and functionality. Moreover, tensile properties reinforcement can be achieved due to the nanoreinforcement role of the SDs. Increased hydrophobicity is also expected from the incorporated hydrophobic moiety, which addresses a key challenge in developing films derived from natural polymers like polysaccharides.

2. Materials and methods

2.1. Materials

Curcumin (65 % purity) from Sigma-Aldrich (Saint Louis, MO, USA), KC from Acros Organics (Geel, Belgium), polysorbate 80 (Tween 80) from Panreac Quimica S.L.U (Barcelona, Spain), and absolute ethanol (99.8 %) from Honeywell (Seelze, Germany) were used to prepare the SDs. Glycerol (99.5 %), sourced from Scharlab (Barcelona, Spain), was used as a plasticizer for KC film preparation. For curcumin release tests, soybean oil from Thermo Scientific (Waltham, MA, USA), acetic acid (99 %), and absolute ethanol (99.8 %) from Sigma-Aldrich (Darmstadt, Germany) were used. Extra-virgin olive oil from a local supermarket was used in the proof of concept. To determine peroxide value (PV), chloroform from Honeywell (Seelze, Germany), glacial acetic acid from Honeywell (Seelze, Germany), potassium iodide from Absolve (Lisbon, Portugal), sodium thiosulphate from Pronalab (Lisbon, Portugal), and potato starch from Panreac Quimica S.L.U (Barcelona, Spain) were used.

Potassium persulfate (99 %), Hl (37 %), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H2O$) (98–102 %) and iron (II) sulphate heptahydrate ($FeSO_4 \cdot 7H2O$) (99 %), purchased from Sigma-Aldrich (Darmstadt, Germany), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) (98 %) provided from Thermo Scientific (Waltham, MA, USA) and TPTZ (2,4,6-tripyridyl-*s*-triazine) (99 %) from TCI Europe (Zwijndrecht, Belgium), were applied in the antioxidant activity determination. For the antimicrobial assessment, the bacterial cultures comprised *Escherichia coli* ATCC 8739 and *Listeria monocytogenes* ATCC 19111, purchased from Scharlab (Barcelona, Spain) and DSMZ (Brunsvique, Germany), respectively. The microorganisms' substrates, brain-heart infusion (BHI) broth, and nutrient agar were acquired from Liofilchem (Roseto degli Abruzzi, Italy). Sodium chloride was purchased from Panreac (Barcelona, Spain).

2.2. Preparation of the curcumin-SDs

Curcumin-SDs were prepared in a previous work of the group, where the effect of using different natural polymers and preparation conditions (pH) was studied [28]. Among the formulations, SDs produced with KC under natural pH (6.18) were selected. Through differential scanning calorimetry and X-ray diffraction, curcumin amorphization and consequent water solubility improvement (19.67 ± 2.29 μg/mL at 25 °C compared to the free curcumin (< 1 μg/mL)) were reported. The curcumin content of this formulation was 0.115 g curcumin/g of SDs. These SDs are characterized by an orange hue (L* = 72.46 ± 0.04, a* = 18.34 ± 0.25, b* = 85.82 ± 0.06; CIELAB space) and median sizes (D50) of 0.403 and 1.710 μm, in number and volume, respectively, determined by laser diffraction using distilled water as the dispersant medium.

2.3. Preparation of the curcumin-SDs functionalized films

The films were prepared using the casting method. KC at 2.5 % (*w*/w) was dissolved in distilled water at 90 °C with stirring, then mixed with glycerol (30 % wt., KC-basis) and SDs (0, 1, 5, 10, 15, and 20 % wt., KC-basis). The corresponding curcumin content in the films was 0, 0.89, 4.42, 8.81, 13.16, and 17.48 mg/g. 25 mL of the solution was poured into a 9 cm diameter Petri dish and left to dry in an oven at 30 °C for 12 h. The final SD-based films were labeled "KCX," with "X" representing the SD percentage (0, 1, 5, 10, 15, or 20). For example, KC20 respects the film with 20 % SDS.

2.4. Physical, optical, and tensile properties of the films

The films (KC0-KC20) were characterized concerning thickness, color attributes, optical transparency, water solubility (WS), water vapor permeability (WVP), water contact angle (WCA), and tensile properties.

The thickness of the films was evaluated at room temperature using a digital micrometer (806.B 25, Facom), averaging six measurements performed in different parts of the films.

The film's color was determined using a Konica Minolta Sensing Inc. CR-400 model colorimeter (Sakai-ku, Japan). All the measurements (L*, a*, and b* (CIELAB space)) were performed in triplicate. RGB color was generated using a free online converter ("Convert EasyRGB," n.d.).

Optical transparency was determined by UV–Vis (V-730 UV–visible Spectrophotometer, Tokyo, Japan). For that, transmittance was scanned from 400 to 700 nm using film samples of 2 × 3 cm^2, and the value at 600 nm was considered for the determination according to Guzman-Puyol and authors [34]. Transparent materials have about 80 % transmittance, while opaque materials have <10 %. Translucent materials fall between 10 % and 80 % transmittance. All the measurements were done in triplicate.

WS was determined following the methodology of Velásquez and authors [12]. The procedure involved drying 2 × 2 cm^2 film pieces at 40 °C for 1 h. After cooling to room temperature, the samples were weighed (W_0) and soaked in 100 mL of distilled water for 24 h. After drying at 100 °C until they reached a constant weight, the samples were weighed again (W_1), and water solubility (WS) was calculated using Eq. (1).

$$WS(\%) = \frac{(W_0 - W_1)}{W_0} \times 100 \tag{1}$$

WVP was measured using the ASTM E96–95 method. Vessels of 3 cm diameter were filled with distilled water to ¾ full and sealed with the films. The vessels were weighed, placed in a desiccator with silica gel for 24 h, and then weighed at 1-h intervals up to 8 h. The water vapor transmission rate (WVTR) was calculated using Eq. (2).

$$WVTR = \frac{G}{t \times A} \tag{2}$$

where G/t expresses the weight loss per unit of time (g/h), and A is the area of the vessel's mouth (m^2). The obtained WVTR values were used to calculate the WVP using Eq. (3).

$$WVP = \frac{WVTR \times Th}{\Delta P} \tag{3}$$

where Th is the film thickness (mm), and ΔP is the partial pressure difference between the two sides of the film (kPa). To calculate this parameter, the relative humidity was assumed to be 100 % on the inner surface of the film and 0 % on the outer surface (25 °C).

WCA was determined using a goniometer/tensiometer (model 210, Ramé-hart, United States). The films were cut into 1.5 × 1.5 cm^2 squares, and contact angle measurements were conducted by depositing a 5 μL sessile drop of distilled water onto the film surface using a high-precision injector. The DROPimage Pro software automatically recorded the contact angle values. Measurements were taken in triplicate using independent samples, and the results are presented as average contact angles over 0 to 60 s, along with the standard deviation.

Tensile properties were determined using a Shimadzu Autograph AGS-X Series tensile tester (Kyoto, Japan) with a 10 kN load cell and non-pneumatic clamps. Five replicas (2 × 3 cm^2) were considered at a crosshead speed of 2 mm/min. Stress-strain curves were generated, and tensile modulus, yield strength, stress at break, and strain at break were determined.

2.5. Surface and cross-section morphology of the films

Micrographs of the films (KC0, KC5, and KC10) were taken using a scanning electron microscope (SEM) (JSM-6610LV, JEOL, Tokyo, Japan) as described by Álvarez and authors [35]. Before analysis, the films were lyophilized and cut into 1 × 1 cm^2 squares. These samples were mounted on aluminum stubs and coated with gold. They were examined vertically for cross-sections and horizontally for surface views using a microscope set to 20 kV.

2.6. Curcumin release studies in stimulated food media

Curcumin release was tested following ASTM D4754–98. Films (KC0, KC5, and KC10) were cut into 1.5 × 1.5 cm^2 pieces and immersed in 22.5 mL (5 mL/cm^2) of various food simulants: semi-fatty (50 % ethanol), fatty (soybean oil), aqueous (10 % ethanol), and acidic (3 % acetic acid), as per Regulation (EU) No. 10/2011. Samples were stored in the dark at 4 °C, and curcumin release was tracked by measuring absorbance at 425 nm at different time intervals in the range of 0 to 2940 min to cover the initial release and the behavior over an extended period. After each measurement, the solution was returned to the vial to keep the volume constant. A calibration curve was generated for curcumin concentrations ranging from 2 to 10 μg/L ($y = 0.1435\times - 0.0175$, $R^2 = 0.9965$), prepared using a 50 % ethanolic aqueous solution (*v*/v) as the solvent. Five mathematical models (zero-order, first-order, Higuchi, Ritger-Peppas, and Fick's diffusion) were used to analyze the release data (see supplementary material; Eq. S1 to Eq. S5).

2.7. Antioxidant activity of the films

The antioxidant activity was tested using the ferric reducing antioxidant power (FRAP) and ABTS radical scavenging assays. First, 150 mg of the films (KC0, KC5, and KC10) were mixed with 5 mL of a 50 % ethanol solution and stirred at 500 rpm in the dark for 24 h. The supernatants were then collected and diluted to 5, 10, 15, and 20 mg/mL to form the film solutions.

The ABTS radical cation decolorization assay was performed as described by Kevij and coauthors [36]. First, a stock solution was made by mixing 7 mM ABTS and 2.45 mM potassium persulfate, then stirred for 16 h in the dark at room temperature. The solution was then diluted with distilled water to reach an absorbance of 0.7 ± 0.04 at 734 nm. Next, 100 μL of the film solutions were combined with 3900 μL of the diluted ABTS solution and kept in the dark at room temperature (20 min). Absorbance was measured at 734 nm. A control was made with 100 μL of 50 % ethanol instead of the film solutions. The ABTS radical scavenging activity (%) was calculated using Eq. (4).

$$Antioxidant\ activity = (A_c - A_s)/A_c \times 100 \tag{4}$$

where A_c is the absorbance of the control, and A_s is the absorbance of the film solutions.

The FRAP assay was performed according to Benzie and Strain [37]. First, a stock solution of 300 mM acetate buffer (pH 3.6), 10 mM TPTZ (2,4,6-tripyridyl-*s*-triazine) in 40 mM HCl, and 20 mM $FeCl_3 \cdot 6H_2O$ in distilled water were prepared. Then, a working solution (FRAP solution) was prepared right before the assay by mixing 10 mL of TPTZ solution, 10 mL of $FeCl_3 \cdot 6H_2O$ solution, and 100 mL of acetate buffer. 100 μL of the film solutions were mixed with 2900 μL of the FRAP solution, vortexed, and left in the dark at room temperature for 30 min. A control was made with 100 μL of distilled water instead of the film solutions. The absorbance was measured at 593 nm. A calibration curve was created with $FeSO_4$ solutions ranging from 50 to 1000 μM.

2.8. Evaluation of olive oil preservation

The oxidative stability of the oil was assessed using a method adapted from existing literature [38,39]. Briefly, test tubes lined with the films (KC0, KC5, and KC10) were filled with 10 mL of olive oil. A control, namely a tube with no film, was also prepared. The tubes were placed in an oven (Vacucell 22, MMM Medcenter, Munich, Germany) at 60 °C for 6 days to simulate accelerated oxidation. The peroxide value (PV, mEqO2/Kg) was measured every 2 days, following European Union standard methods (Annex III of EEC/2568/91 Regulation and amendments). Approximately 2 g of sample were dissolved in a mixture containing 15 mL of glacial acetic acid and 10 mL of chloroform, followed by adding 1 mL of saturated aqueous potassium iodide solution. The flask was sealed and kept in the dark for 5 min at room temperature (20 °C). Subsequently, 75 mL of distilled water were added, followed by a few drops of a 1 % starch solution (indicator, *w/v*). The released iodine was titrated with a 0.01 N sodium thiosulphate standard solution. A blank was performed for each laboratory session. PV values were calculated using Eq. (5):

$$PV = V \times T \times 1000/m \tag{5}$$

where V is the volume of sodium thiosulphate in mL after the blank correction, N is the exact normality of the sodium thiosulphate solution, and m is the sample mass in grams.

2.9. Antibacterial activity

Bacterial cultures of *Escherichia coli* ATCC 8739 and *Listeria monocytogenes* ATCC 19111, stored at −70 °C (ThermoFisher, STP, AS), were activated in BHI broth and incubated at 37 °C for 24 h (Raypa, Incutterm, Barcelona, Spain). The inoculum was then prepared in BHI broth or saline solution, adjusting the cell density to 1.5×10^6 cells/mL using a densitometer (DEN-1 McFarland densitometer, Grant-bio, UK) set at 550 nm. The films' antibacterial activity, including their bacteriostatic effect, was determined according to Lluberas and authors [40]. Two approaches were used: reduction and inhibition. The effectiveness of the films against the selected strains was measured by counting viable cells and colony-forming units (CFU).

For the inhibition test, 4.5 mL of BHI broth with 10 % of the standardized inoculum was prepared; then, 0.25 mL was applied to 1.5×1.5 cm^2 film pieces placed in the center of Petri dishes. Filter paper of the same dimensions was used as the control. The plates were incubated in an oven at 37 °C for 0, 60, and 120 min and then lixiviated with 2 mL of sterile distilled water. The pure lixiviate and serial dilutions (0.1 mL) were spread onto Petri dishes with a solid culture medium (nutrient agar for *Escherichia coli* and BHI for *Listeria monocytogenes*). The plates were incubated at 37 °C for 24 h before cell counting. For the reduction test, 4.5 mL of saline solution with 10 % of the standardized inoculum was prepared. Then, all the previously described steps were applied.

2.10. Statistical analysis

For all assays, when replicas were performed, results were expressed as the average ± standard deviation. When applied, the results were analyzed using one-way analysis of variance (ANOVA), and the significant differences between the averages were determined using Tukey's test (α = 0.05), performed in Statistica StatSoft Inc. (2011) (version 10, Tulsa, OK, USA).

3. Results and discussion

3.1. Physical, optical, and tensile properties of the films

Table 1 shows the thickness, color parameters (L*, a*, and b*), RGB colors, visual appearance (photographic images), and transparency of the films (KC0-KC20). For the curcumin-functionalized films, thickness ranged from 85 to 90 μm, which was consistent but slightly lower than the KC0 film (100 μm). All films except KC0 were yellow due to the added curcumin-SDs. The L* value, which measures lightness on a scale from zero to 100 (where zero is black and 100 is white), decreased from KC1 to KC20. The a* value, which represents the red-green balance (positive for red and negative for green), increased with positive values. The b* coordinate, indicating the yellow-blue balance (positive for yellow and negative for blue), rose from KC1 to KC10, then decreased for KC15 and KC20, remaining positive throughout. The same behavior in the color parameters was reported by Roy and Rhim [19] in their investigation of carbohydrate composite films functionalized with curcumin. Concerning transparency, films with >10 % SDs were visually opaque (transmittance <10 %), whereas the other formulations, including KC0, were translucent (10 % < transmittance <80 %). Adding SDs to films reduced transparency from 71.38 % (KC0) to 5.02 % (KC20). In summary, uniform color distribution was observed in this work, improving the product's appearance and showing that curcumin is evenly spread throughout the film, guaranteeing uniform bioactivity across the packaging material. The translucent to opaque nature of the films may pose a limitation for packaging applications [41].

Water resistance and vapor permeability are crucial parameters for food packaging since they help predict shelf life, ensuring proper use [42]. Preventing moisture ingress or egress helps avoid unwanted chemical reactions, mitigating undesirable odors, flavors, or spoilage [43]. The film's WS, WVP, and WCA values are reported in Table 2. For WS, the values ranged from 82.33 % to 84.86 %, except for KC10, which had a significantly lower value of 77.18 %. Similar results were reported for carrageenan-based films, with WS values of 87.30 % for KC films containing curcumin and 81.38 % for iota-carrageenan films blended with cassava starch [19,44]. Moreover, a comparable decrease in WS from 82.60 % to 76.60 % was reported for KC-based films incorporated with olive leaf extract [45]. The observed trend aligns with the WCA results, where KC10 displayed the highest value (47.36°), indicating enhanced water resistance, even though still pointing out a hydrophilic character (values below 90°). Nonetheless, incorporating curcumin-SDs positively correlates with increased water resistance, a characteristic that should be further enhanced in these natural-based film solutions. Due to their hydrophilic nature, high WS and low WCA values are common in films made from polysaccharides and proteins.

Packaging preserves food and extends shelf life, preventing moisture loss or absorption from poor seals, holes, or water vapor permeation [46]. WVP measures the rate at which water vapor passes through the packaging material due to differences in relative humidity. Studies have shown that adding active compounds to films affects WVP. Typically, hydrophobic compounds make films less absorbent, improving their barrier against water vapor. Hydrophilic compounds help the film retain moisture, reducing WVP by trapping water molecules. WVP is also affected by factors like the material's thickness; thicker materials generally have lower WVP values, indicating better resistance to water vapor transmission [45]. The WVP results for the KC0 film and formulations with SDs were similar, ranging from $2.86 \cdot 10^{-10}$ to $3.20 \cdot 10^{-10}$ $g \cdot m/s \cdot m^2 \cdot Pa$, showing no significant differences, suggesting that adding SDs did not affect this parameter. The determined values align with other studies, where values of 2.03×10^{-10} $g \cdot m/s \cdot m^2 \cdot Pa$ [47] and 2.38×10^{-10} $g \cdot m/s \cdot m^2 \cdot Pa$ [48] were found for KC-based films with similar polymer and glycerol concentrations.

Creating films with suitable tensile properties ensures they

Table 1
Thickness, color parameters (L*, a*, b*), RGB color, visual appearance, and transparency of the films.

Sample	Thickness (µm)	Color				Visual appearance	Transparency (%T_{600})
		L*	a*	b*	RGB		
KC0	100.00 ± 7.07 ^{a}	90.46 ± 0.03 ^{a}	0.77 ± 0.01 ^{e}	-1.55 ± 0.08 ^{e}			71.66 ± 0.76 ^{a}
KC1	89.17 ± 2.04 ^{b}	84.70 ± 0.18 ^{b}	-0.99 ± 0.03 ^{f}	18.13 ± 0.18 ^{d}			68.63 ± 0.43 ^{b}
KC5	85.83 ± 2.04 ^{b}	74.23 ± 0.06 ^{c}	6.51 ± 0.33 ^{d}	57.48 ± 0.41 ^{c}			40.95 ± 0.27 ^{c}
KC10	85.00 ± 4.47 ^{b}	64.11 ± 0.26 ^{d}	21.52 ± 0.28 ^{c}	67.62 ± 0.58 ^{a}			13.96 ± 0.19 ^{d}
KC15	85.00 ± 4.47 ^{b}	58.47 ± 0.38 ^{e}	25.72 ± 0.32 ^{b}	59.86 ± 0.81 ^{b}			8.19 ± 0.10 ^{e}
KC20	90.00 ± 3.16 ^{b}	57.27 ± 0.73 ^{f}	28.84 ± 0.65 ^{a}	57.74 ± 0.85 ^{c}			5.12 ± 0.19 ^{f}

Results are presented as average ± standard deviation. Different letters in each column correspond to significant differences (α = 0.05).

Table 2
Water solubility (WS), water vapor permeability (WVP), and water contact angle (WCA) of the films.

Sample	WS (%)	WVP (10^{-10} g · m/ s · m^2 · Pa)	WCA (°)
KC0	82.89 ± 0.87 ^{b,c}	2.97 ± 8.93·10^{-12} ^{a}	43.09 ± 1.05 ^{a,b}
KC1	84.86 ± 1.17 ^{a}	2.83 ± 1.88·10^{-11} ^{a}	42.19 ± 3.44 ^{a,b}
KC5	83.69 ± 0.91 ^{a,b}	2.91 ± 1.97·10^{-11} ^{a}	39.06 ± 2.20 ^{b}
KC10	77.18 ± 0.64 ^{d}	2.96 ± 3.71·10^{-12} ^{a}	47.36 ± 0.93 ^{a}
KC15	83.67 ± 1.13 ^{b}	2.86 ± 7.51·10^{-10} ^{a}	45.51 ± 3.43 ^{a,b}
KC20	82.33 ± 1.16 ^{c}	3.20 ± 3.40·10^{-11} ^{a}	41.71 ± 0.87 ^{b}

Results are presented as average ± standard deviation. Different letters in each column correspond to significant differences (α = 0.05).

effectively protect the food, maintaining its integrity through the supply chain until reaching the consumer [43,49]. Fig. 1 shows the stress-strain curves for the films, and Table 3 summarizes the obtained values for tensile modulus, yield strength, and stress and strain at break. The

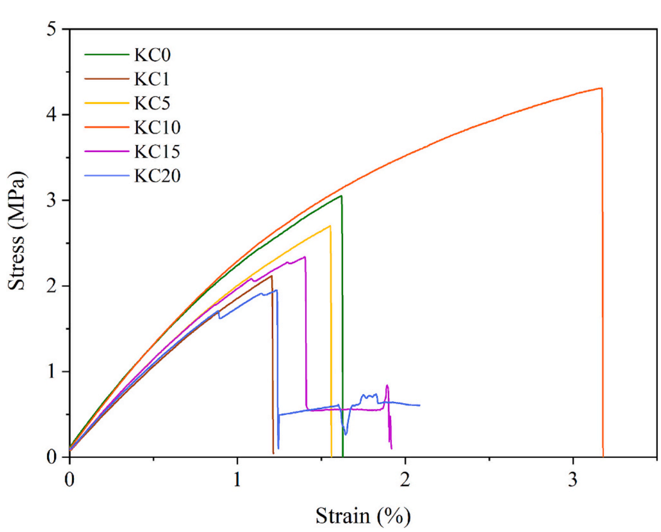

Fig. 1. Stress-strain curves of the films KC0-KC20.

Table 3
Tensile modulus, yield strength, stress, and strain at the break of the films KC0-KC20.

Sample	Tensile modulus (MPa)	Yield strength (MPa)	Stress at break (MPa)	Strain at break (%)
KC0	214.62 ± 11.44 ^{a,b}	2.57 ± 0.25 ^{a}	3.37 ± 0.86 ^{a}	2.26 ± 0.88 ^{a}
KC1	186.34 ± 10.65 ^{b}	1.91 ± 0.25 ^{a}	2.10 ± 0.22 ^{b}	1.36 ± 0.19 ^{a}
KC5	207.41 ± 24.03 ^{a,b}	2.25 ± 0.42 ^{a}	2.50 ± 0.43 ^{a,b}	1.48 ± 0.08 ^{a}
KC10	241.47 ± 28.13 ^{a}	2.40 ± 0.76 ^{a}	3.50 ± 0.98 ^{a}	2.36 ± 1.19 ^{a}
KC15	187.36 ± 15.52 ^{b}	2.10 ± 0.36 ^{a}	2.20 ± 0.37 ^{b}	1.31 ± 0.23 ^{a}
KC20	185.26 ± 7.03 ^{b}	1.80 ± 0.23 ^{a}	1.91 ± 0.21 ^{b}	1.18 0.10 ^{a}

Results are presented as mean ± standard deviation. Different letters in each column correspond to significant differences (α = 0.05).

tensile modulus quantifies the material's stiffness in the elastic region. Yield strength indicates the maximum stress a material can handle before it starts to deform permanently. The breaking point refers to the stress and strain values when the material breaks [50,51].

The tensile modulus (214.62 MPa) and strain at break (2.26 %) for KC0 were consistent with values reported for films made from similar KC concentration solutions, which were 218.5 MPa and 2.33 %, respectively [47]. Curcumin incorporation generally led to a slight decrease in tensile properties. An exception was noted for the KC10 sample, which, even not statistically different from KC0, showed improved tensile properties, including higher tensile modulus (12.51 % increase), stress (3.86 % increase), and strain at break (4.42 % increase). This effect may arise from a good distribution of curcumin in the KC matrix, which enhanced tensile properties due to stronger hydrogen bonds between KC and the curcumin-SDs [25]. The intensification of hydrogen bonding between the KC and curcumin-SDs was also corroborated by FTIR (broadening of the OH peak), even though no conclusive effect of concentration impact was perceived (see Fig. S2 in supplementary material). In the case of yield strength, there was a 6.61 % decrease with no significant difference from KC0.

When compared to commercial packaging materials, the tensile properties of KC films are generally inferior to those of commonly used materials like amorphous polyethylene terephthalate (A-PET), which is typically used in olive oil bottles. A-PET typically exhibits a tensile modulus of 2500 MPa, yield strength of approximately 55 MPa, a stress at break exceeding 55 MPa, and a strain at break >25 % [52]. However, despite their inferior tensile properties, studies have shown that films with lower tensile properties, such as poultry and fish gelatin, are still suitable for applications like single-dose sachets [53]. This indicates that while the KC films may not fully meet commercial standards for bottle packaging, they could still be effective for specific uses, such as internal coatings for transparent olive oil bottles, where they can help reduce oxidation, extend shelf life, and preserve the packaging's aesthetic appeal.

Since the KC10 film showed the best tensile properties and water resistance, followed by KC5, these two samples, along with KC0 as a reference, were chosen for the subsequent studies.

3.2. Surface and cross-section morphology of the films

Fig. 2 displays the surface and cross-section morphology of the films analyzed by SEM. Overall, the films have a uniform structure despite some visible roughness. Similar observations were reported for KC films without additives [54] and for KC films added with pomegranate flesh and peel extracts [55]. In the present work, SDs can be perceived in KC5 and KC10 film surfaces as visible rod-like or ellipsoidal entities, which increased as SD content increased, impacting the internal structure of the films, as observed in the cross-section images. The KC5 film showed an irregular internal structure, namely by presenting fissures. KC10 exhibited a more compact structure due to the higher SDs content, which correlates with increased stiffness, as supported by the observed rise in tensile modulus and stress at break.

3.3. Curcumin release studies in stimulated food media

The release profile and kinetics of active compounds in different media can be predicted using established models [56]. In this work, multiple food media simulants, including fatty (soybean oil), semi-fatty (50 % ethanol), aqueous (10 % ethanol), and acidic (3 % acetic acid, pH < 4.5) media, were studied over 50 h. The results are shown in Fig. 3. During the testing period, no curcumin was released into the fatty stimulant medium. In the semi-fatty medium, curcumin release reached 95 % for KC5 and 96 % for KC10 films, whereas in the aqueous medium, only 4.12 % (KC5) and 4.15 % (KC10) were released. In the acidic medium, values of 6.09 % (KC5) and 3.57 % (KC10) were achieved. Generally, the films showed an initial burst release, associated with the curcumin at the film's surface, followed by a sustained release until reaching a plateau, similar to what was observed in films made of tara gum and polyvinyl alcohol loaded with curcumin [57].

The correlation coefficient R^2 for the evaluated release models (Zero-order, First-order, Higuchi, Ritger-Peppas, and Fick models), along with the release exponent n (Ritger-Peppas model) and the diffusion coefficient D (Fick diffusion model) are summarized in Table S1 (supplementary material). In the Ritger-Peppas model, an $n \leq 0.5$ indicates a Fickian diffusion mechanism, while $n > 0.5$ indicates a non-Fickian mechanism. Values between 0.5 and 1.0 reflect an anomalous transport and a release influenced by diffusion and swelling. An n value of 1 suggests that the release is governed by the swelling and relaxation of polymer chains, and $n > 1.0$ represents extreme transport, where the polymeric matrix undergoes breakdown [56]. In the Fick model, the diffusion coefficient (D) indicates the rate at which curcumin diffuses through the film's matrix into the surrounding medium [58].

The first-order model best described the release in the semi-fatty medium (R^2 0.994 for both KC5 and KC10). KC5 was also well represented by the Ritger-Peppas (R^2 0.992) and KC10 by the Higuchi and Fick models (R^2 of 0.998 and 0.991, respectively). The Fick model was the best for the aqueous medium for both samples, with R^2 and D values

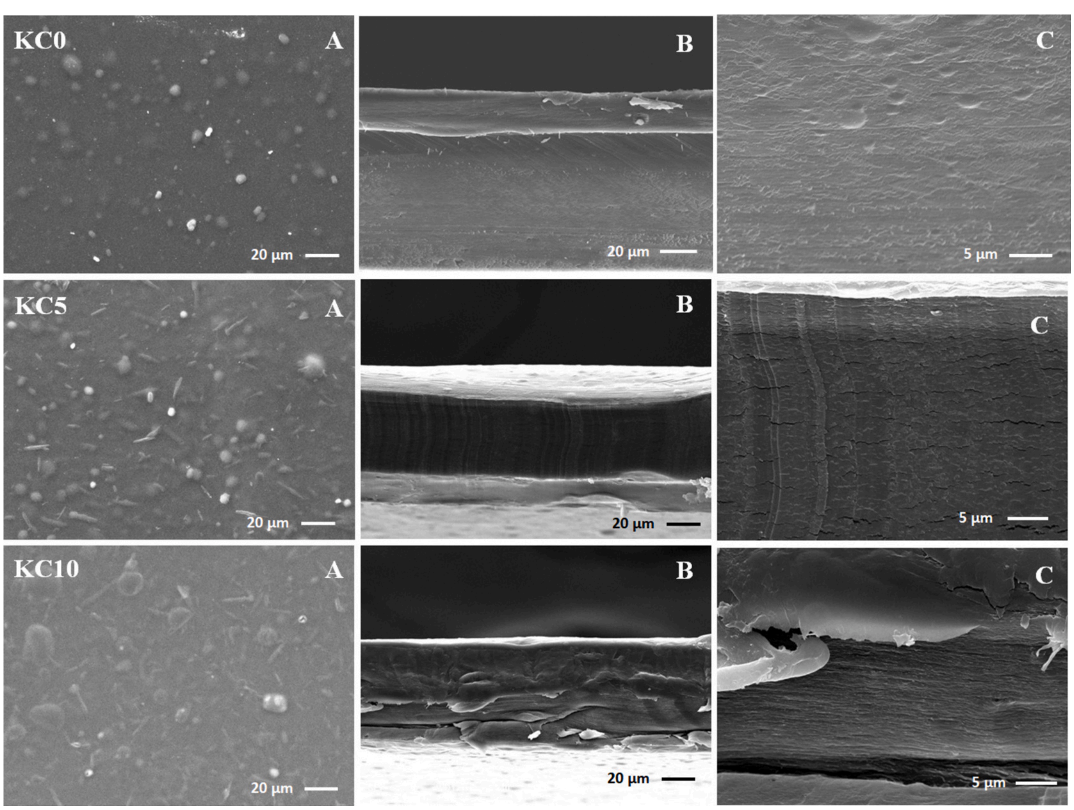

Fig. 2. SEM images of surface (A) and cross-section (B, C) of the films at x600, x600 and x3000 magnifications, respectively.

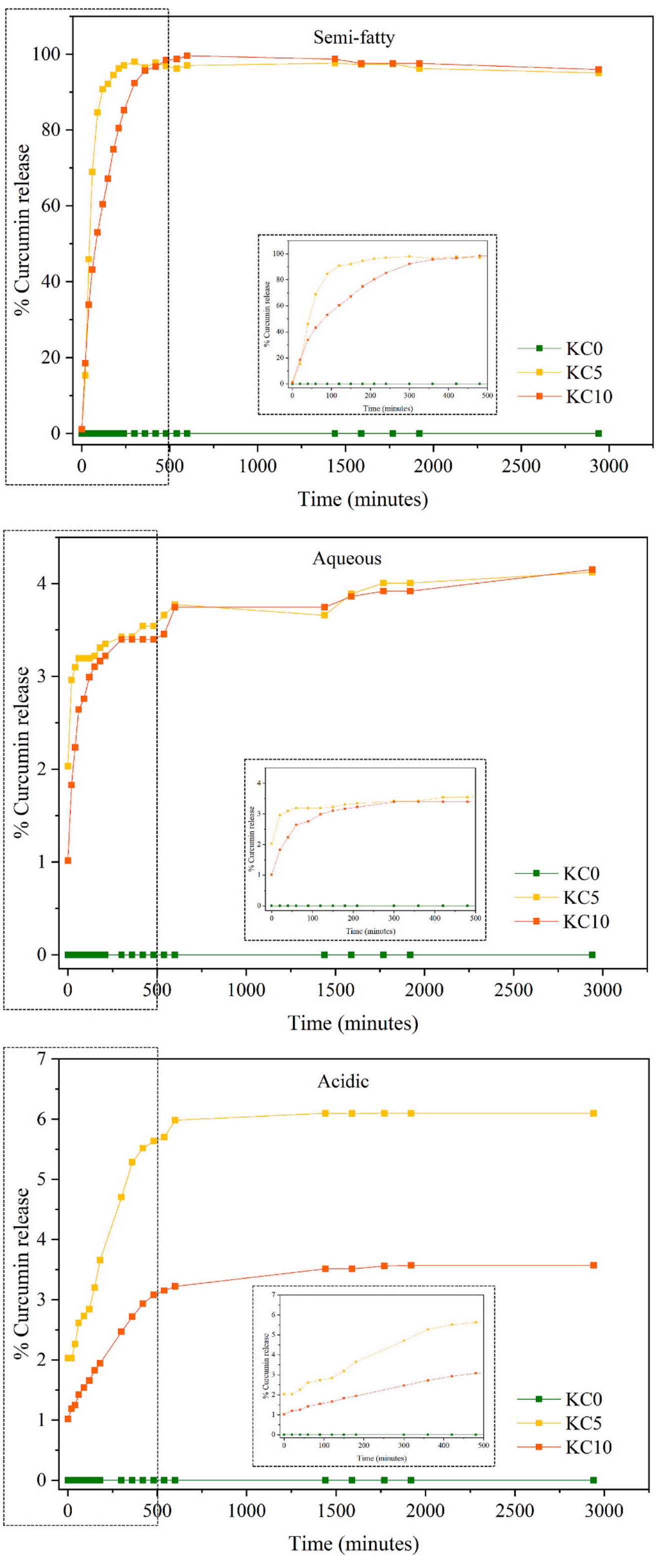

Fig. 3. Curcumin release in food simulant media: semi-fatty (A), aqueous (B), and acidic (C).

of 0.983 and $1.21{\cdot}10^{-12}$ for KC5 and 0.982 and $6.72{\cdot}10^{-13}$ for KC10. The Ritger-Peppas model pointed out for Fickian diffusion ($n \leq 0.5$) for KC5, where solvent transport occurs at a rate significantly faster than polymeric chain relaxation. For KC10, a non-Fickian or anomalous transport was found ($0.5 < n < 1.0$), i.e., curcumin was released by diffusion and swelling at similar rates for both mechanisms [56]. In an acidic medium, the curcumin release for KC5 fitted well both the Fick (R^2 0.992 and D $4.27{\cdot}10^{-12}$) and the zero-order (R^2 0.985) models. In the case of KC10, Ritger-Peppas (R^2 of 0.988 and $n > 1$) and the first order (R^2 of 0.981) worked well. For $n > 1$, the water sorption process induces tension, leading to film breaking and, thus, to a burst release. Considering that these values represent extreme release behaviors, the Ritger-Peppas model is believed to be the most suitable for describing the observed sample behavior.

3.4. *Antioxidant activity*

Oxidation is considered one of the major causes of food deterioration and quality loss. Developing packaging materials that protect food products from oxidation while preserving their sensory qualities is an important research area [59]. This can be done using materials functionalized with curcumin, a powerful antioxidant [60]. Curcumin exhibits potent antioxidant activity by scavenging reactive oxygen species (ROS) like superoxide radicals, hydrogen peroxide, and nitric oxide (NO), as well as enhancing antioxidant enzymes such as SOD, CAT, GPx, and OH-1, which are critical for preventing lipid peroxidation [61]. It also inhibits enzymes like LOX, COX, and iNOS, reducing oxidative stress and inflammation [62]. Fig. 4 summarizes these mechanisms and includes the FRAP and ABTS assays used to assess curcumin's antioxidant activity.

The produced films (KC5, KC10, and KC0) were analyzed, and the results of the ABTS and FRAP tests are represented graphically in Fig. 5. In both tests, the film without curcumin (KC0) showed no antioxidant activity. Films with curcumin exhibited significantly improved antioxidant capacity, which increased with curcumin concentration; i.e., according to both methods, the film with the highest antioxidant capacity was KC10. These findings suggest that the functionalized films can effectively prevent or slow down the oxidation of fats and oils in packaged foods, fulfilling the goal of the work. By inhibiting lipid oxidation, the films help maintain the freshness and quality of food products, reducing off-flavors and rancidity [63].

3.5. *Evaluation of olive oil preservation*

Taking into account the curcumin release profiles obtained from the incorporated SDs films, which show no release in a fatty simulating

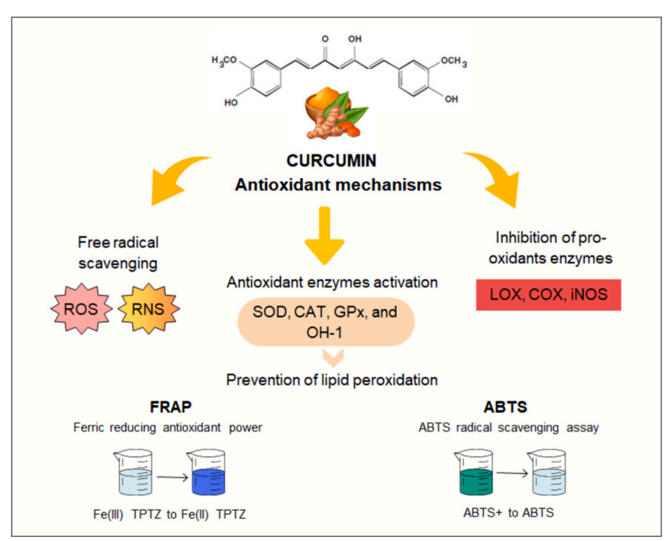

Fig. 4. Mechanistic aspects of curcumin's antioxidant actions, along with representations of the FRAP and ABTS assays. ROS: reactive oxygen species, RNS: reactive nitrogen species, SOD: superoxide dismutase, CAT: catalase, GPx: glutathione peroxidase, OH-1: heme Oxygenase-1, LOX: lipooxygenase, COX: cyclooxygenase, iNOS: inducible nitric oxide synthase.

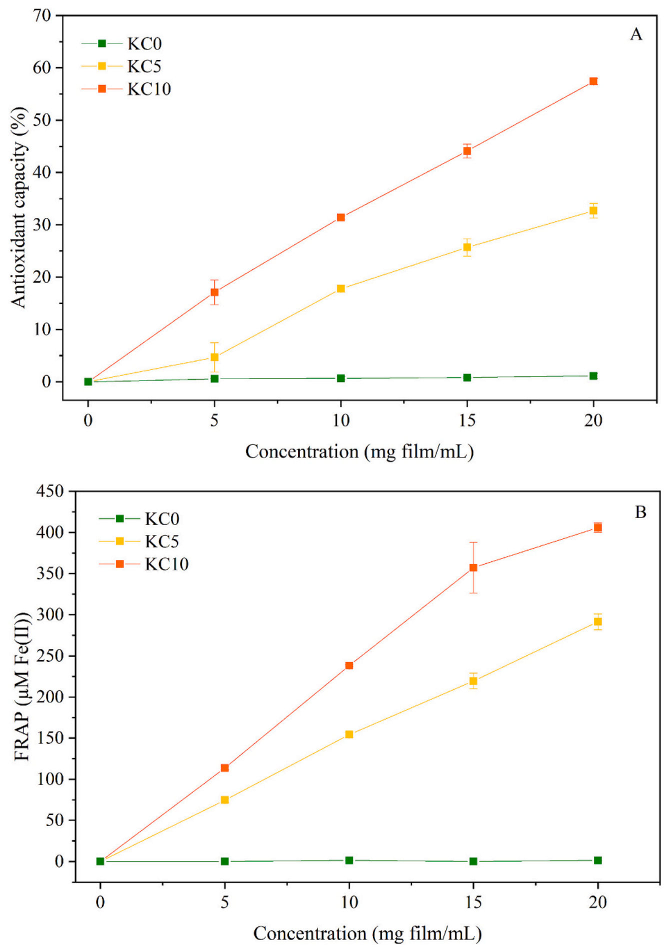

Fig. 5. Antioxidant properties of films: ABTS (A) and FRAP (B).

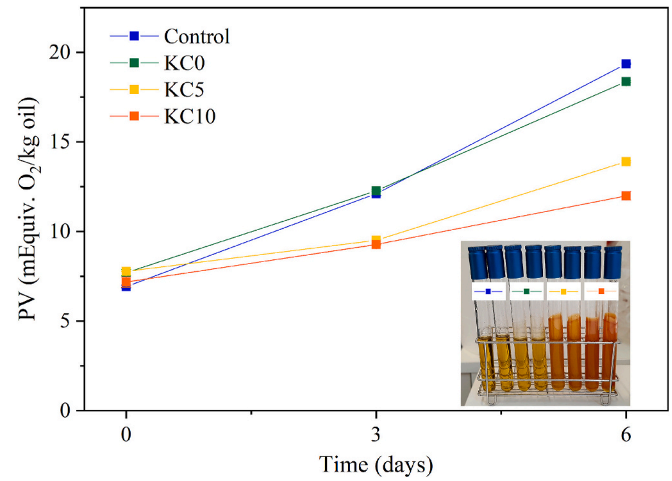

Fig. 6. Peroxide value of olive oil with films for 6 days.

medium, addressing a significant concern regarding compound transfer from the packaging to the food products, extra virgin olive oil was selected as the food matrix for the proof-of-concept using KC5, KC10, and KC0. Lipid-rich foods, such as dairy products, nuts, and oils, are particularly prone to oxidation during storage. Oxygen, light, and heat lead to the breakdown of fatty acids, forming free radicals, hydroperoxides, and secondary volatile compounds that produce an unpleasant "rancid" taste and odor. As a result, the oil's overall quality deteriorates [64,65], with antioxidants helping slow down this reaction by neutralizing the free radicals [66]. In this context, curcumin-SDs as antioxidants for oil packaging can offer enhanced protection and extend the shelf life of olive oil. The applicable EU legislation concerning the characteristics of olive oil and olive oil residues (European Community Regulation EEC/2568/91 from 11th July and amendments) defines extra virgin olive oil requirements as free acidity (FA, in % of oleic acid) $\leq$ 0,8 and PV $\leq$ 20 (mEq. O_2/kg oil).

The olive oil oxidative stability was monitored for 6 days under accelerated oxidation conditions. The obtained PV values (mEq. O_2/kg oil) and an image showing the used experimental setup are presented in Fig. 6. At time 0, all the samples showed similar peroxide values of 7 mEq O_2/kg oil, indicating that the selected commercial olive oil met appropriate quality standards. After three days under accelerated oxidative conditions, the control (tube with no film) and the tube with KC0 presented higher PV values ($\sim$ 12 mEq. O_2/kg oil) compared to the KC5 and KC10 films ($\sim$ 9 mEq. O_2/kg oil). After 6 days, the control and the KC0 sample presented values reaching 20 mEq. O_2/kg oil (the maximum value allowed by regulations to ensure quality standards), while KC5 and KC10 samples were below these limits (14 and 12 mEq O_2/kg oil, respectively). These outcomes demonstrated that both KC5 and KC10 effectively extended the quality of olive oil, with slightly better results for KC10. Accelerated oxidation at 60 °C can be used to estimate the storage time under normal conditions, where one day at 60 °C is roughly equivalent to 16 days at 20 °C or 8.79 days at 25 °C [67,68], predicting for the studied case a preservation time of at least 96 days under ambient storage conditions (20 °C). Overall, these results corroborate curcumin's excellent stability under accelerated testing conditions.

3.6. Antibacterial activity

The antibacterial activity of the most promising KC film (KC10) was compared to KC0 and filter paper (control) against *Escherichia coli* and *Listeria monocytogenes*, common food-borne pathogenic bacteria. Fig 7 summarizes the obtained results. After 120 min, the KC0 film reduced bacterial growth by 42.7 % for the gram-negative *Escherichia coli* and 15.7 % for the gram-positive *Listeria monocytogenes*, compared to the control. In contrast, the KC10 film showed significantly higher inhibition, with reductions of 78.4 % for *Escherichia coli* and 78.0 % for *Listeria monocytogenes*. KC10 demonstrated a notable increase in inhibition compared to KC0 and the control after 120 min. However, at the 60-min mark, the number of viable cells was still higher. Literature reports that KC films exhibit bacteriostatic properties, particularly against *Escherichia coli* [69,70], which justifies the results obtained for KC0. Nevertheless, curcumin, well-known for its antimicrobial activity [22,71], enhanced this effect.

Unlike nutrient-rich media like BHI, the saline solution used in the reduction approach prevents bacterial growth while maintaining osmotic balance, supporting survival and avoiding osmotic shock or dehydration [72]. This behavior was confirmed by the stable CFU count in the control over the evaluation period. In contrast, the CFU count decreased gradually for both KC0 and KC10 films, indicating their bacteriostatic effect. Although both films showed promising results against the tested bacteria, incorporating curcumin-SDs into the films yielded significantly improved results, with statistically significant differences observed at 60 and 120 min. KC0 caused reductions of 87.7 % for *Escherichia coli* and 63.1 % for *Listeria monocytogenes* after 120 min, whereas for the KC10, 95.4 % and 90.6 % were found, respectively.

In a recent study by Velásquez and coauthors [12], KC films enriched with honey and bee pollen phenolic compounds resulted in enhanced antibacterial activity. No significant differences were observed between the KC film added with the free extract and the control (no added extract), even though a slight reduction in bacterial growth was observed. In another study, adding curcumin to KC films reduced the bacterial growth rate for the same strains used in the present work. When added to chitosan films, curcumin accelerated bacterial reduction

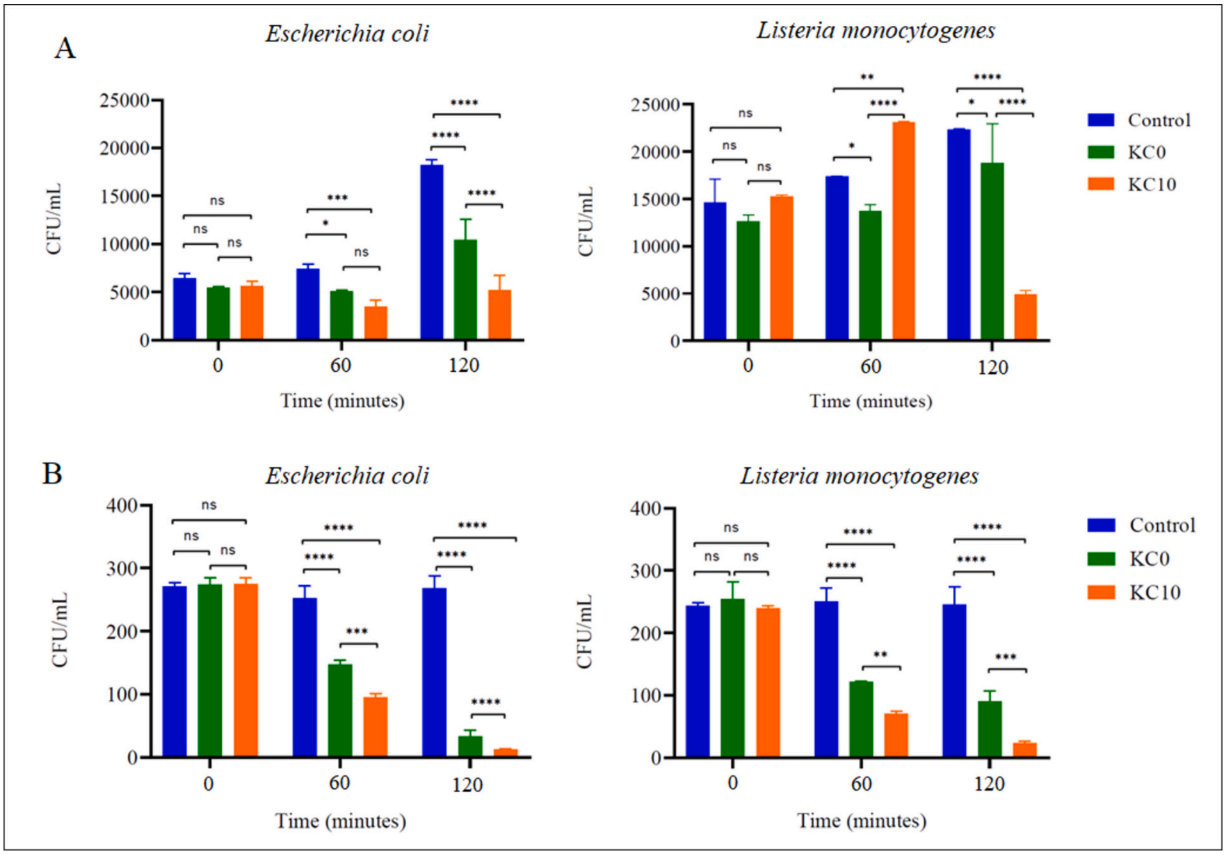

Fig. 7. Antibacterial activity of the films following inhibition (A) and reduction (B) mechanisms for the two studied bacteria (*Escherichia coli* and *Listeria monocytogenes*).

[19]. In this work, the KC0 film (no added curcumin-SDs) exhibited moderate antibacterial activity in both studied approaches, inhibition, and reduction. The film added with curcumin-SDs (KC10) exceeded KC0 effect. The antibacterial activity of KC is attributed to the sulfate groups in the polymer, whereas curcumin disrupts FtsZ, a key protein in bacterial cell division, leading to abnormalities that inhibit bacterial growth and proliferation [73].

4. Conclusions

Curcumin, known for its potent antioxidant and antimicrobial properties, shows considerable potential for food preservation. However, its high hydrophobicity makes it challenging to incorporate into hydrophilic matrices, rendering it less suitable for natural polymer-based packaging materials, typically hydrophilic. This study demonstrates that curcumin-SD (solid dispersion) systems can address this challenge effectively, providing several additional benefits. Compared to the base KC films (without curcumin), KC films functionalized with 10 % curcumin-SDs exhibited better water resistance, similar water vapor permeability, improved tensile properties, and enhanced antioxidant and antibacterial performance. Furthermore, the curcumin-SD KC films exhibited unique behaviors in food simulants, highlighting the role of SDs during film incorporation (compatibilization) and in influencing curcumin release characteristics. Overall, the developed packaging material effectively prevented olive oil oxidation (rancidity) while avoiding curcumin migration into the oil, thus supporting a non-migratory active protection mechanism. Though viewed as less desirable, the observed color and opacity can benefit olive oil packaging by protecting against light exposure. This study highlights the benefits of curcumin-SDs, yet it is worth studying the long-term stability of these materials beyond accelerated test conditions. Enhancing film hydrophobicity through optimized curcumin-SD strategies also presents valuable potential for further advancements in this field. As an extension of this work, other hydrophobic compounds can be explored to functionalize hydrophilic polymeric matrices.

CRediT authorship contribution statement

Stephany Cunha de Rezende: Writing – original draft, Methodology, Investigation, Conceptualization. **Arantzazu Santamaria-Echart:** Writing – review & editing, Supervision, Conceptualization. **Heloísa Helena Scorsato Almeida:** Methodology, Investigation. **Ismael Marcet:** Methodology, Investigation, Conceptualization. **Maria Carpintero:** Methodology, Investigation. **Manuel Rendueles:** Writing – review & editing. **Mary Lopretti:** Methodology, Investigation. **Madalena Maria Dias:** Writing – review & editing, Supervision. **Maria Filomena Barreiro:** Writing – review & editing, Supervision, Resources, 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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P/0007/2020); LSRE-LCM UIDB/50020/2020 (DOI:10.54499/UIDB/50020/2020) and UIDP/50020/2020 (DOI:10.54499/UIDP/50020/2020); and ALiCE LA/P/0045/2020 (DOI:10.54499/LA/P/0045/2020). FCT for the PhD research grants of Stephany C. de Rezende (DOI:10.54499/SFRH/BD/147326/2019) and Heloísa Helena Scorsato de Almeida (DOI:10.54499/SFRH/BD/148124/2019). Arantzazu Santamaria-Echart thanks the FCT for the National funding for scientific employment through the institutional program contract. Red CYTED ENVABIO100 121RT0108.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijbiomac.2024.138446.

References

[1] J.G. de Oliveira Filho, M.R.V. Bertolo, M.Á.V. Rodrigues, C.A. Marangon, G. da C. Silva, F.C.A. Odoni, M.B. Egea, Curcumin: a multifunctional molecule for the development of smart and active biodegradable polymer-based films, Trends Food Sci. Technol. 118 (2021) 840–849, https://doi.org/10.1016/j.tifs.2021.11.005.

[2] M. Asgher, S.A. Qamar, M. Bilal, H.M.N. Iqbal, Bio-based active food packaging materials: sustainable alternative to conventional petrochemical-based packaging materials, Food Res. Int. 137 (2020) 109625, https://doi.org/10.1016/j.foodres.2020.109625.

[3] W. Grzebieniarz, D. Biswas, S. Roy, E. Jamróz, Advances in biopolymer-based multi-layer film preparations and food packaging applications, Food Packag. Shelf Life 35 (2023) 101033, https://doi.org/10.1016/j.fpsl.2023.101033.

[4] W. Yin, C. Qiu, H. Ji, X. Li, S. Sang, D.J. McClements, A. Jiao, J. Wang, Z. Jin, Recent advances in biomolecule-based films and coatings for active and smart food packaging applications, Food Biosci. 52 (2023) 102378, https://doi.org/10.1016/j.fbio.2023.102378.

[5] A. Manzoor, B. Yousuf, J.A. Pandith, S. Ahmad, Plant-derived active substances incorporated as antioxidant, antibacterial or antifungal components in coatings/films for food packaging applications, Food Biosci. 53 (2023) 102717, https://doi.org/10.1016/j.fbio.2023.102717.

[6] S.A.A. Mohamed, M. El-Sakhawy, M.A.M. El-Sakhawy, Polysaccharides, protein and lipid -based natural edible films in food packaging: a review, Carbohydr. Polym. 238 (2020) 116178, https://doi.org/10.1016/j.carbpol.2020.116178.

[7] B. Rukmanikrishnan, S. Ramalingam, S.S. Kim, K. Jaewoong, Rheological and anti-microbial study of silica and silver nanoparticles-reinforced k-carrageenan/hydroxyethyl cellulose composites for food packaging applications, Cellulose 28 (2021) 5577–5590, https://doi.org/10.1007/s10570-021-03873-z.

[8] R. Venkatesan, N. Rajeswari, T.T. Thiyagu, Preparation, characterization and mechanical properties of k-Carrageenan / SiO 2 nanocomposite films for antimicrobial food, Bull. Mater. Sci. 40 (2017) 609–614. doi:https://doi.org/10.1007/s12034-017-1403-3.

[9] C. Santos, A. Ramos, Â. Luís, M.E. Amaral, Production and characterization of k-carrageenan films incorporating Cymbopogon winterianus essential oil as new food packaging materials, Foods 12 (2023), https://doi.org/10.3390/foods12112169.

[10] L.Y. Maroufi, M. Ghorbani, M. Tabibiazar, M. Mohammadi, A. Pezeshki, Advanced properties of gelatin fi lm by incorporating modi fi ed kappa-carrageenan and zein nanoparticles for active food packaging, Int. J. Biol. Macromol. 183 (2021) 753–759, https://doi.org/10.1016/j.ijbiomac.2021.04.163.

[11] A. Farhan, N. Mohd, Active edible fi lms based on semi-re fi ned κ -carrageenan : antioxidant and color properties and application in chicken breast packaging, Food Packag. Shelf Life 24 (2020) 100476, https://doi.org/10.1016/j.fpsl.2020.100476.

[12] P. Velásquez, G. Montenegro, L.M. Valenzuela, A. Giordano, G. Cabrera-Barjas, O. Martin-Belloso, K-carrageenan edible films for beef: honey and bee pollen phenolic compounds improve their antioxidant capacity, Food Hydrocoll. 124 (2022) 107250, https://doi.org/10.1016/j.foodhyd.2021.107250.

[13] J.G. Oliveira Filho, M.B. Egea, Edible Bioactive Film with Curcumin: A Potential "Functional" Packaging?, Int. J. Mol. Sci. 23 (2022) 5638. doi:https://doi.org/10.3390/ijms23105638.

[14] N. Li, X. Yang, D. Lin, Development of bacterial cellulose nanofibers/konjac glucomannan-based intelligent films loaded with curcumin for the fresh-keeping and freshness monitoring of fresh beef, Food Packag. Shelf Life 34 (2022) 100989, https://doi.org/10.1016/j.fpsl.2022.100989.

[15] Y. Liu, Y. Ma, Y. Liu, J. Zhang, M.A. Hossen, D.E. Sameen, J. Dai, S. Li, W. Qin, Fabrication and characterization of pH-responsive intelligent films based on carboxymethyl cellulose and gelatin/curcumin/chitosan hybrid microcapsules for pork quality monitoring, Food Hydrocoll. 124 (2022) 107224, https://doi.org/10.1016/j.foodhyd.2021.107224.

[16] E. Kaya, L.N. Kahyaoglu, G. Sumnu, Development of curcumin incorporated composite films based on chitin and glucan complexes extracted from Agaricus bisporus for active packaging of chicken breast meat, Int. J. Biol. Macromol. 221 (2022) 536–546, https://doi.org/10.1016/j.ijbiomac.2022.09.025.

[17] X. Zhai, X. Wang, J. Zhang, Z. Yang, Y. Sun, Z. Li, X. Huang, M. Holmes, Y. Gong, M. Povey, J. Shi, X. Zou, Extruded low density polyethylene-curcumin film: a hydrophobic ammonia sensor for intelligent food packaging, Food Packag. Shelf Life 26 (2020) 100595, https://doi.org/10.1016/j.fpsl.2020.100595.

[18] J. Liu, H. Wang, P. Wang, M. Guo, S. Jiang, X. Li, S. Jiang, Films based on κ-carrageenan incorporated with curcumin for freshness monitoring, Food Hydrocoll. 83 (2018) 134–142, https://doi.org/10.1016/j.foodhyd.2018.05.012.

[19] S. Roy, J.W. Rhim, Preparation of carbohydrate-based functional composite films incorporated with curcumin, Food Hydrocoll. 98 (2020), https://doi.org/10.1016/j.foodhyd.2019.105302.

[20] F. He, Q. Kong, Z. Jin, H. Mou, Developing a unidirectionally permeable edible film based on κ -carrageenan and gelatin for visually detecting the freshness of grass carp fillets, Carbohydr. Polym. 241 (2020) 116336, https://doi.org/10.1016/j.carbpol.2020.116336.

[21] J. Chen, Y. Zheng, Q. Kong, Z. Sun, X. Liu, A Wechat miniprogram (' Fresh color') based on smart phone to indicate the freshness of Atlantic salmon (*Salmo salar* L .) and oysters on site by detection of the color changes of curcumin films, Food Control 145 (2023) 109520, https://doi.org/10.1016/j.foodcont.2022.109520.

[22] N. Aliabbasi, M. Fathi, Z. Emam-Djomeh, Curcumin: a promising bioactive agent for application in food packaging systems, J. Environ. Chem. Eng. 9 (2021) 105520, https://doi.org/10.1016/j.jece.2021.105520.

[23] H. Tambawala, S. Batra, Y. Shirapure, A.P. More, Curcumin- a bio-based precursor for smart and active food packaging systems: a review, J. Polym. Environ. 30 (2022) 2177–2208, https://doi.org/10.1007/s10924-022-02372-x.

[24] J. Wu, J. Li, F. Xu, A. Zhou, S. Zeng, B. Zheng, S. Lin, Effective preservation of chilled pork using photodynamic antibacterial film based on curcumin-β-Cyclodextrin complex, Polymers (Basel) 15 (2023) 1023, https://doi.org/10.3390/polym15041023.

[25] D. Lai, F. Zhou, A. Zhou, S.S. Hamzah, Y. Zhang, J. Hu, S. Lin, Comprehensive properties of photodynamic antibacterial film based on κ-carrageenan and curcumin-β-cyclodextrin complex, Carbohydr. Polym. 282 (2022) 119112, https://doi.org/10.1016/j.carbpol.2022.119112.

[26] Y. Han, M. Zhou, D. Julian, F. Liu, C. Cheng, J. Xiong, M. Zhu, S. Chen, Investigation of a novel smart and active packaging materials: nanoparticle-filled carrageenan-based composite films, Carbohydr. Polym. 301 (2023) 120331, https://doi.org/10.1016/j.carbpol.2022.120331.

[27] S. Pan-On, W. Tiyaboonchai, Development, characterization and Caco-2 cells absorption of curcumin solid dispersion for oral administration, J Drug Deliv Sci Technol 86 (2023) 104574, https://doi.org/10.1016/j.jddst.2023.104574.

[28] S.C. de Rezende, O. Ferreira, A. Santamaria-Echart, M.M. Dias, M.F. Barreiro, Evaluating the potential of natural polymers for water-dispersible curcumin-based solid dispersion colourant systems for food applications, J. Food Eng. 371 (2024) 111986, https://doi.org/10.1016/j.jfoodeng.2024.111986.

[29] V.F. Leimann, O.H. Gonçalves, G.D. Sorita, S. Rezende, E. Bona, I.P.M. Fernandes, I.C.F.R. Ferreira, M.F. Barreiro, Heat and pH stable curcumin-based hydrophylic colorants obtained by the solid dispersion technology assisted by spray-drying, Chem. Eng. Sci. 205 (2019) 248–258, https://doi.org/10.1016/j.ces.2019.04.044.

[30] K. Kaewkroek, A. Petchsomrit, A. Wira Septama, R. Wiwattanapatapee, Development of starch/chitosan expandable films as a gastroretentive carrier for ginger extract-loaded solid dispersion, Saudi Pharmaceutical Journal 30 (2022) 120–131, https://doi.org/10.1016/j.jsps.2021.12.017.

[31] W. Siripruekpong, O. Issarachot, K. Kaewkroek, R. Wiwattanapatapee, Development of Gastroretentive carriers for curcumin-loaded solid dispersion based on expandable starch/chitosan films, Molecules 28 (2023) 361, https://doi.org/10.3390/molecules28010361.

[32] A. Salevic, C. Prieto, L. Cabedo, V. Nedovi, J.M. Lagaron, Physicochemical, Antioxidant and antimicrobial properties of electrospun poly (ε -caprolactone) films containing a solid dispersion of sage (Salvia officinalis L.) extract, Nanomaterials 9 (2019) 270, https://doi.org/10.3390/nano9020270.

[33] F. Wang, J. Zhan, R. Ma, Y. Tian, Simultaneous improvement of the physical and biological properties of starch films by incorporating steviol glycoside-based solid dispersion, Carbohydr. Polym. 311 (2023) 120766, https://doi.org/10.1016/j.carbpol.2023.120766.

[34] S. Guzman-Puyol, J.J. Benítez, J.A. Heredia-Guerrero, Transparency of polymeric food packaging materials, Food Res. Int. 161 (2022) 111792, https://doi.org/10.1016/j.foodres.2022.111792.

[35] S. Álvarez, S. Weng, C. Álvarez, I. Marcet, M. Rendueles, M. Díaz, A new procedure to prepare transparent, colourless and low-water-soluble edible films using blood plasma from slaughterhouses, Food Packag. Shelf Life 28 (2021) 100639, https://doi.org/10.1016/j.fpsl.2021.100639.

[36] H. Taghavi Kevij, M. Salami, M. Mohammadian, M. Khodadadi, Fabrication and investigation of physicochemical, food simulant release, and antioxidant properties of whey protein isolate-based films activated by loading with curcumin through the pH-driven method, Food Hydrocoll. 108 (2020) 106026, https://doi.org/10.1016/j.foodhyd.2020.106026.

[37] I.F.F. Benzie, J.J. Strain, The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": the FRAP assay, Anal. Biochem. 239 (1996) 70–76, https://doi.org/10.1006/abio.1996.0292.

[38] S.S. de Campos, A. de Oliveira, T.F.M. Moreira, T.B.V. da Silva, M.V. da Silva, J. A. Pinto, A.P. Bilck, O.H. Gonçalves, I.P. Fernandes, M.F. Barreiro, F. Yamashita, P. Valderrama, M.A. Shirai, F.V. Leimann, TPCS/PBAT blown extruded films added with curcumin as a technological approach for active packaging materials, Food Packag. Shelf Life 22 (2019) 100424, https://doi.org/10.1016/j.fpsl.2019.100424.

[39] M. Carpintero, I. Marcet, M. Rendueles, M. Díaz, Egg yolk oil as a plasticizer for Polylactic acid films, Membranes (Basel) 12 (2022) 46, https://doi.org/10.3390/membranes12010046.

[40] G. Lluberas, D. Batista-Menezes, J.M. Zuñiga-Umaña, G. Montes de Oca-Vásquez, N. Lecot, J.R. Vega-Baudrit, M. Lopretti, Biofilms Functionalized Based on Bioactives and Nanoparticles with Fungistatic and Bacteriostatic Properties for

Food Packing Uses, in: Biology and Life Sciences Forum, MDPI AG, 2023: p. 10. doi:https://doi.org/10.3390/blsf2023028010.

[41] P. Cazón, M. Vázquez, G. Velazquez, Cellulose-glycerol-polyvinyl alcohol composite films for food packaging: evaluation of water adsorption, mechanical properties, light-barrier properties and transparency, Carbohydr. Polym. 195 (2018) 432–443, https://doi.org/10.1016/j.carbpol.2018.04.120.

[42] R. Puscaselu, G. Gutt, S. Amariei, Rethinking the future of food packaging: biobased edible films for powdered food and drinks, Molecules 24 (2019), https://doi.org/10.3390/molecules24173136.

[43] F. Versino, F. Ortega, Y. Monroy, S. Rivero, O.V. López, M.A. García, Sustainable and bio-based food packaging: a review on past and current design innovations, Foods 12 (2023) 1057, https://doi.org/10.3390/foods12051057.

[44] D. Praseptiangga, D. Widyaastuti, C.P. And, I.M. Joni, Development and characterization of semi-refined iota carrageenan/SiO2-ZnO bionanocomposite film with the addition of cassava starch for application on minced chicken meat packaging Danar, Foods 10 (2021) 1–15, https://doi.org/10.3390/foods10112776.

[45] T.R. Martiny, V. Raghavan, C.C. de Moraes, G.S. da Rosa, G.L. Dotto, Bio-based active packaging: carrageenan film with olive leaf extract for lamb meat preservation, Foods 9 (2020) 1–14, https://doi.org/10.3390/foods9121759.

[46] S. Rawdkuen, A. Faseha, S. Benjakul, P. Kaewprachu, Application of anthocyanin as a color indicator in gelatin films, Food Biosci. 36 (2020), https://doi.org/10.1016/j.fbio.2020.100603.

[47] G.A. Paula, N.M.B. Benevides, A.P. Cunha, A. Vit, S. Morais, H.M.C. Azeredo, A.M. B. Pinto, Development and characterization of edible films from mixtures of k -carrageenan, i -carrageenan , and alginate 47 (2015) 140–145, https://doi.org/10.1016/j.foodhyd.2015.01.004.

[48] S. Shojaee-Aliabadi, H. Hosseini, M.A. Mohammadifar, A. Mohammadi, M. Ghasemlou, S.M. Hosseini, R. Khaksar, Characterization of κ-carrageenan films incorporated plant essential oils with improved antimicrobial activity, Carbohydr. Polym. 101 (2014) 582–591, https://doi.org/10.1016/j.carbpol.2013.09.070.

[49] V. Gupta, D. Biswas, S. Roy, A comprehensive review of biodegradable polymer-based films and coatings and their food packaging applications, Materials 15 (2022) 5899, https://doi.org/10.3390/ma15175899.

[50] S. Mangaraj, A. Yadav, L.M. Bal, S.K. Dash, N.K. Mahanti, Application of biodegradable polymers in food packaging industry: a comprehensive review, J Packag Technol Res 3 (2019) 77–96, https://doi.org/10.1007/s41783-018-0049-y.

[51] K.K. Sadasivuni, P. Saha, J. Adhikari, K. Deshmukh, M.B. Ahamed, J.J. Cabibihan, Recent advances in mechanical properties of biopolymer composites: a review, Polym. Compos. 41 (2020) 32–59, https://doi.org/10.1002/pc.25356.

[52] Angst+Pfister APSOplast® PET-A Amorphous PET, (n.d.). https://www.matweb.com/search/DataSheet.aspx?MatGUID=1171e477d91a44c8a817e27f0ff3061a (accessed November 29, 2024).

[53] A. Ashrafi, H. Babapour, S. Johari, F. Alimohammadi, F. Teymori, A.M. Nafchi, N. N. Shahrai, N. Huda, A. Abedinia, Application of poultry gelatin to enhance the physicochemical, mechanical, and rheological properties of fish gelatin as alternative mammalian gelatin films for food packaging, Foods 12 (2023), https://doi.org/10.3390/foods12030670.

[54] M.A. Abu-Saied, M. Elnouby, T. Taha, M. El-Shafeey, A.G. Alshehri, S. Alamri, H. Alghamdi, A. Shati, S. Alrumman, M. Al-Kahtani, M. Moustafa, Potential decontamination of drinking water pathogens through k-carrageenan integrated green bottle fly bio-synthesized silver nanoparticles, Molecules 25 (2020) 1936, https://doi.org/10.3390/molecules25081936.

[55] Y. Liu, X. Zhang, C. Li, Y. Qin, L. Xiao, J. Liu, Comparison of the structural, physical and functional properties of κ-carrageenan films incorporated with pomegranate flesh and peel extracts, Int. J. Biol. Macromol. 147 (2020) 1076–1088, https://doi.org/10.1016/j.ijbiomac.2019.10.075.

[56] M.L. Bruschi, Mathematical models of drug release, in: Strategies to Modify the Drug Release from Pharmaceutical Systems, 2015: pp. 63–86. doi:https://doi.org/10.1016/b978-0-08-100092-2.00005-9.

[57] Q. Ma, Y. Ren, L. Wang, Food hydrocolloids investigation of antioxidant activity and release kinetics of curcumin from tara gum/polyvinyl alcohol active film, Food Hydrocoll. 70 (2017) 286–292, https://doi.org/10.1016/j.foodhyd.2017.04.018.

[58] D.E. El-nashar, N.N. Rozik, A.M. Soliman, F. Helaly, Study the release kinetics of curcumin released from PVA/curcumin composites and its evaluation towards hepatocarcinoma, J Appl Pharm Sci 6 (2016) 67–72, https://doi.org/10.7324/JAPS.2016.60710.

[59] H. Kumar, A. Ahuja, A.A. Kadam, V.K. Rastogi, Y.S. Negi, Antioxidant film based on chitosan and Tulsi essential oil for food packaging, Food Bioprocess Technol. 16 (2023) 342–355, https://doi.org/10.1007/s11947-022-02938-6.

[60] K. Jakubczyk, A. Drużga, J. Katarzyna, K. Skonieczna-żydecka, Antioxidant potential of curcumin—a meta-analysis of randomized clinical trials, Antioxidants 9 (2020) 1–13, https://doi.org/10.3390/antiox9111092.

[61] J. Sharifi-Rad, Y. El Rayess, A.A. Rizk, C. Sadaka, R. Zgheib, W. Zam, S. Sestito, S. Rapposelli, K. Neffe-Skocińska, D. Zielińska, B. Salehi, W.N. Setzer, N.S. Dosoky, Y. Taheri, M. El Beyrouthy, M. Martorell, E.A. Ostrander, H.A.R. Suleria, W.C. Cho, A. Maroyi, N. Martins, Turmeric and its major compound curcumin on health: bioactive effects and safety profiles for food, Pharmaceutical, Biotechnological and Medicinal Applications, Front Pharmacol 11 (2020) 01021, https://doi.org/10.3389/fphar.2020.01021.

[62] M. Wojtyłko, P. Kunstman, H. Bartylak, Ł. Raszewski, T. Osmałek, A. Froelich, A well-known plant and new therapeutic strategies: turmeric and its components in Oral inflammatory diseases treatment, Appl. Sci. 13 (2023) 7809, https://doi.org/10.3390/app13137809.

[63] S. Roy, J.W. Rhim, Preparation of antimicrobial and antioxidant gelatin/curcumin composite films for active food packaging application, Colloids Surf. B: Biointerfaces 188 (2020) 110761, https://doi.org/10.1016/j.colsurfb.2019.110761.

[64] D. Nogueira, N.S. Marasca, J.M. Latorres, J.A.V. Costa, V.G. Martins, Effect of an active biodegradable package made from bean flour and açaí seed extract on the quality of olive oil, Polym. Eng. Sci. 62 (2022) 1070–1080, https://doi.org/10.1002/pen.25907.

[65] N. Rodrigues, S. Casal, A.M. Peres, P. Baptista, J.A. Pereira, Seeking for sensory differentiated olive oils? The urge to preserve old autochthonous olive cultivars, Food Research International 128 (2020) 108759 https://doi.org/10.1016/j.foodres.2019.108759.

[66] R.K. Deshmukh, K.K. Gaikwad, Natural antimicrobial and antioxidant compounds for active food packaging applications, Biomass Convers. Biorefinery (2022), https://doi.org/10.1007/s13399-022-02623-w.

[67] P.L. López, M.A. Marchesino, N.R. Grosso, R.H. Olmedo, Comparative study of accelerated assays for determination of equivalent days in the shelf life of roasted high oleic peanuts: chemical and volatile oxidation indicators in accelerated and room temperature conditions, Food Chem. 373 (2022), https://doi.org/10.1016/j.foodchem.2021.131479.

[68] Z. He, S. Nam, K.T. Klasson, Oxidative stability of cottonseed butter products under accelerated storage conditions, Molecules 28 (2023), https://doi.org/10.3390/molecules28041599.

[69] F. Wang, Z. Yao, H. Wu, N. Zhu, X. Gai, Antibacterial activities of kappa-carrageenan oligosaccharides *, Appl. Mech. Mater. 108 (2012) 194–199, https://doi.org/10.4028/www.scientific.net/AMM.108.194.

[70] S. Yamashita, Y. Sugita-Konishi, M. Shimizu, In vitro Bacteriostatic Effects of Dietary Polysaccharides (2001), https://doi.org/10.3136/fstr.7.262.

[71] A. Adamczak, M. Ożarowski, T.M. Karpiński, Curcumin, a natural antimicrobial agent with strain-specific activity, Pharmaceuticals 13 (2020) 1–12, https://doi.org/10.3390/ph13070153.

[72] C. Wei, X. Zhao, Induction of viable but Nonculturable Escherichia coli O157:H7 by low temperature and its resuscitation, Front. Microbiol. 9 (2018) 1–9, https://doi.org/10.3389/fmicb.2018.02728.

[73] M. Fujimori, H. Sogawa, S. Ota, P. Karpov, S. Shulga, Y. Blume, N. Kurita, Specific interactions between mycobacterial FtsZ protein and curcumin derivatives : molecular docking and ab initio molecular simulations, Chem. Phys. Lett. 692 (2018) 166–173, https://doi.org/10.1016/j.cplett.2017.12.045.