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ORIGINAL PAPER

Radiation Synthesis of Edible Coating Films of Nanocurcumin Based on Carboxymethyl Chitosan/Polyvinyl Alcohol to Extend the Shelf Life of Sweet Orange "Valencia"

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Abstract
Edible coating CMCS/PVA/Cur and films were prepared using γ-irradiation to extend the shelf-life of sweet orange "Valencia" fruits. Water-soluble CMCS was synthesized by carboxymethylation of chitosan. Extraction of curcumin from turmeric powder and conversion to Cur-NPs of 76–108 nm average size was achieved. CMCS/PVA/Cur membranes were prepared via the casting method and gamma-irradiation technique. The chemical properties were studied by FTIR and XRD as well as studying the effect of irradiation dose on gel content, water swelling, and mechanical properties. FTIR and XRD results confirm the interaction between functional groups of Cur-NPs with CMCS/PVA polymer chains. Results indicated that the membrane possessed good tensile strength and gel content of 97.4% and the swelling was significantly decreased with increasing the irradiation dose. Fruits were dipped in CMCS/PVA/Cur coatings at different concentrations of Cur-NPs (0, 2.5, 5, and 10%) and stored at room temperature of 65–70% RH for about 70 days. The efficiency of coatings was assessed by decay (%), weight loss (%), pH, vitamin C content, total soluble solids (TSS), titratable acidity (TA), and TSS/TA ratio. Quality characteristics of coated fruits were better than uncoated fruits especially the coating solution of 2.5% Cur-NPs provides accepted freshness and quality. No decay was noticed for the coated fruits till 56 days, whereas the control exhibited decay of 36%. The prepared coating solutions possessed good antimicrobial activity and cytocompatibility characteristics and showed normal viability even at all concentrations. Results demonstrated a promising packaging material to extend the shelf life and freshness of orange fruits.

Keywords Carboxymethyl chitosan · Curcumin nanoparticles · Gamma irradiation · Edible coating · Sweet orange "Valencia" · Shelf life

Introduction

Citrus fruits of the family Rutaceae include several fruits for instance oranges, mandarins, limes, lemons, sour oranges, and grapefruits have received much attention due to their antioxidant activity and high contents of bioactive molecules such as ascorbic acid, carotenoids, flavonoids, and phenolic compounds [1]. Egypt produces more than 2.9 million tons of total citrus fruits annually, which is equivalent to approximately 69% of the total production of citrus fruits, and the exported quantity of Egyptian oranges is estimated at 30% of the total Egyptian fruit exports. Among the most important varieties of oranges that are produced and exported in large quantities in Egypt are the navel orange and Valencia orange [2–5]. Valencia Oranges (*Citrus sinensis* (L.) Osb.) are one of the most important export varieties (1.43 million tons) due to their medium sizes, high quality, and the high percentage of juice, which contains a high percentage of Vitamin C [2]. The fruits are collected in large quantities that exceed the needs of the markets, so they are stored in refrigerators until they are presented in the markets. The fruit contamination by micro-organisms is usually accelerated in hot climates, especially in relative moisture of high levels. Also, due to the high moisture content in fruits, the growth of various micro-organisms especially in the

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post-harvest period is high. Hence damages induced by pathogens should be reduced by using suitable methods that increase and enhance their resistance to pathogens. Green and blue mold is the most important damage-causing factor in the shelf life period, which is created by *Penicillium digitatum* and *Penicillium italicum*, respectively. The green mold decay usually turns into green in wounded areas but in decay caused by blue mold, the edges of the wound turn into another color [6].

Various methods used to preserve the fruits from spoilage throughout the storage and transportation period by various chemical disinfectants are used to reduce microbes and fungi such as thiabendazole, sodium bicarbonate, benzothiadiazole, beta-aminobutyric acid, and 2,6-dichlorosonicotinic acid, etc. Chemical disinfectants pose a risk to consumer health in the long run, with their high cost and handling risks [7]. Alternatively, some natural waxy materials are also used to advance the appearance of the fruits and reduce weight loss and shrinkage, but it may affect the flavor of the fruits accordingly of the increased secretion of volatile substances associated with anaerobic respiration conditions.

These problems could be solved by applying edible coatings from natural materials and essential oils [8, 9]. An edible coating is one of the effective methods used to improve fruit appearance and prolong the shelf-life stability of fruits during the storage period by preventing gas exchange, controlling the respiration process, limiting mass loss, and declining microorganisms' growth on the surface [10]. Edible coatings seem to be one novel method and the greatest beneficial feature of packaging materials which has been verified to have a positive and safe approach to extending the shelf life of products. This type of coating is made from various natural resources like polysaccharides, (chitosan, carrageenan, alginate, and cyclodextrin), protein, and lipid materials. The edible coating technique is achieved using different components including biopolymers, plasticizers, and other additives of food-grade ingredients. However hydrophobic substances like resins, waxes, or some insoluble, thus the interest in using natural and soluble material are important to avoid using lipids and hydrophobic substances.

One of the most food-grade coating materials which are safe and suitable for their intended use is curcumin. Curcumin (1, 7-bis 4-hydroxy-3-methoxyphenyl-1,6-heptadiene-3,5-dione), isolated from an Indian plant Turmeric (*Curcuma longa* L.) the aromatic rhizome of the ginger family (*Zingiberaceae*) can help preserve food through the preparation of biopolymer films by blending with functional materials such as using Curcumin [11]. Curcumin exhibits many therapeutic properties, including anti-inflammation, anti-oxidation and anti-cancer, and anti-HIV; antimicrobial activities inhibit lipid peroxidation and scavenge superoxide anion, singlet oxygen, nitric oxide, and hydroxyl radicals [12–14]. Despite these advantages, curcumin holds various disadvantages like reduced dissolution and solubility in physiological pH and insufficient bioavailability. These limitations could be solved by converting curcumin to form curcumin nanoparticles (nano-curcumin) (Cur-NPs) [15] which is the best route to get better dissolution, solubility, bioavailability, and enhancement in its surface area when compared to poorly soluble bulk curcumin. In recent years, there is a growing interest in blending curcumin with biopolymers such as cellulose, cellulose acetate, collagen, gelatin, carrageenan, agar, chitosan, and poly(lactic acid) to produce composites with improved functional properties for biomedical application [16–19]. Additionally, several approaches have been established to fabricate nano-sized curcumin, to develop its bioavailability, facilitate its dissolution rate, and increase its surface area as well as enhance chemical and physical stability [20]. Polymer blending of natural and synthetic polymers represents a new class of materials with improved properties and could be called biosynthetic polymeric materials. Several natural polymers such as collagen, chitin, chitosan, starch, cellulose, and pectin could be blended with synthetic polymers such as polyvinyl alcohol (PVA) using different techniques to develop new materials. PVA is a water-soluble synthetic polymer of good film-forming ability and excellent mechanical, thermal, and water resistance [21], biodegradable properties [22–24] and could be used for varied industrial [25] biomedical [26–28], food packaging applications [29, 30]. Chitosan is a cationic natural polymer resulting from the deacetylation of chitin and was used effectively for the preservation of many fruits and vegetables, such as grapes, strawberries, berries, jujube, and fresh-cut lotus root. This is due to its low toxicity biocompatibility, antioxidant, and biological (bacteriostatic and fungistatic) properties [31]. At present, edible coatings based on chitosan as a kind of film-forming biopolymer and as a protective gas barrier with antimicrobial activity to keep the freshness of fruits and extend their shelf life were interesting. Although chitosan has many properties, one major problem is that it is insoluble in a neutral medium. This could be solved by chemical modification of hydroxyl and amino groups and widening its applications [32–35]. Carboxymethylation of chitosan is a good way to prepare carboxymethyl chitosan (CMCS) of good water solubility and widen their use with other materials could be used in several applications of fruits [36–41].

Gamma irradiation is a favorable technology with a single-step process and sterilized simultaneously for the preparation of different kinds of materials, films, and coatings based on biopolymers [42]. This method is economically and technically feasible and physically a safe technique, having a strong antimicrobial effect. The irradiation process is an effective, fast, clean, and well-controlled technique for high-performance applications such as food packaging, preservation, and healthcare fields [43]. This work aims to synthesize

and development of a novel and eco-friendly antimicrobial coating solution and films by blending CMCS/PVA with different ratios of Cur-NPs and enhancing by gamma irradiation to extend the shelf life of Sweet Orange "Valencia" fruit at room temperature and 65–70% relative humidity (RH) for about 70 days. The quality characteristics of all coated fruits such as weight loss percentage, decay percentage, Juiciness, pH, vitamin C, TSS, TA, and TSS/TA ratio were investigated during the storage periods.

Materials and Methods

Materials

Poly(vinyl alcohol) (PVA) of molecular weight 17–18 kDa and 87–89% degree of hydrolysis, glutaraldehyde, dichloromethane, and tween 80 were obtained from Qualikems, India. Chitosan (CS) of molecular weight 420 kDa and degree of deacetylation 85% was obtained from Sigma-Aldrich Co. Monochloroacetic acid, sodium hydroxide, sodium carbonate, 2,6-dichlorophenolindophenol, acetic acid, and ascorbic acid were obtained from SUVCHEM laboratory chemicals.

Fruits of sweet orange "Valencia" were collected manually from the trees of the farms of Al-Shams Group for Advanced Agriculture on the Cairo-Ismailia agricultural road in mid-February 2022. The fruits were free from any postharvest treatment. The fruits were transferred to the laboratory for packaging and storage of horticultural crops at Food Irradiation Department, National Centre for Radiation Research and Technology, Egyptian Atomic Energy Authority, Cairo, Egypt. The fruits were sorted for two days (curing process to lose some of the moisture from fruit peels to produce the infection with fungi) then graded, washed with tap water, and left to dry. Fruits of the same size (medium) were selected and divided into four groups, each group containing three replicates (25 fruits/ replicate).

Extraction of Curcumin from Turmeric powder

Curcumin compound was extracted from turmeric (*Curcuma longa*) roots using the soxhlet apparatus as follows: 50 g turmeric powder was embedded in a porous thimble of Soxhlet apparatus. The ethanol (250 mL) extraction solvent was added and kept the temperature at 60 °C (to avoid dissociation or decomposition of the active ingredients of curcumin) using a heating mantel for 6 h. The soxhlet apparatus was connected with the cooling circulation apparatus to increase the number of the siphon (12 times) during the hour until the yellow color extract was obtained. At the end of the period, the ethanolic extract was filtered and transferred into a rotary evaporator to obtain curcumin powder at 35 °C under a vacuum. The obtained curcumin powder was left at room temperature until complete solvent evaporation and the dried residue of the curcumin compound was obtained [44].

Preparation of Curcumin Nanoparticles (Cur-NPs)

Firstly, 250 mg curcumin powder was dissolved in 50 mL of dichloromethane under magnetic stirring for 15 min. Secondly; the mixture solution was added dropwise to 100 mL boiling distilled water containing 0.5 mL of tween 80 as stabilizing agent with continuous stirring for 1 h. After complete addition, the mixture solution was subjected to sonication for 2 h. After that, the mixture solution was concentrated at 50 °C and then centrifuged at 3000 rpm for 1 h to obtain a clear orange-colored precipitate, and the supernatant was discarded. Finally, the orange-colored residue was dried in an oven to obtain the desired Cur-NPs [45].

Preparation of Carboxymethyl Chitosan (CMCS)

CMCS was prepared from CS as described previously [41, 46, 47]. Briefly, 10 g of CS was added to 150 mL of 50% (w/v) NaOH solution. Then, 100 mL of isopropanol was added while stirring at 50 °C for 1 h. Then, 10 g monochloroacetic acid dissolved in 30 mL isopropanol was gradually added into the alkali CS solution for 30 min. The mixture solution was heated at 50 °C for 4 h. The mixture solution was filtered to separate the solid part. After that, 250 mL of 70% (v/v) methanol was added to the solid part with stirring for 1 h, and then the pH was adjusted to pH 7 by adding glacial acetic acid. Then, the mixture solution was filtered and the resultant solid part (CMCS) was washed with 250 mL of 95% (v/v) methanol and left to dry at 60 °C.

Preparation of CMCS/PVA/Cur Coating Solutions

The coating solutions were prepared by gamma radiation-induced crosslinking reaction of CMCS/PVA polymer blend solutions [30] incorporated with different ratios of Cur-NPs. Three coating solutions of CMCS/PVA/Cur at fixed copolymer concentration (6 wt%), a copolymer composition ratio of CMCS/PVA (50/50 v/v), and varying Cur-NPs ratios. Firstly, 2 g of CMCS was dissolved in 100 mL distilled water with stirring at 50 ℃ for 2 h to obtain a homogenous solution of 2 wt% CMCS. Secondly, 4 g of PVA was dissolved in 100 mL distilled water with stirring at 50 ℃ for 2 h until complete dissolution to get 4 wt% PVA solution. Thirdly, 6 wt% of CMCS/PVA copolymer blend concentration was prepared by slowly incorporating CMCS solution into the PVA solution under stirring at 60 °C until the copolymer blend became homogenous. Fourthly, accurate amounts of Cur-NPs of 2.5, 5 and 10% (relative to CMCS content), exactly 50, 100, and 200 mg, were weighed, dissolved in

5 mL absolute ethanol, and then added to CMCS/PVA mixture solutions under continuous stirring for 2 h until homogeneity. Finally, the CMCS/PVA/Cur reaction mixture solutions were poured into glass bottles, closed, and then exposed to gamma irradiation at the dose of 15 kGy. The irradiation process was done using a ^{60}Co source with a dose rate of 0.833 kGy/h. The irradiation facility is located at the National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority, Cairo, Egypt. After irradiation, the obtained three CMCS/PVA/Cur solutions were used as coating solutions for sweet orange "Valencia" as follows: the first coating solution is CMCS/PVA/Cur-2.5%, the second coating solution is CMCS/PVA/Cur-5% and the third coating solution is CMCS/PVA/Cur-10%. The collected fruits of each group were dipped in the prepared CMCS/PVA/Cur coating solutions for 1 min and then left to dry until a very thin layer was formed around the fruits. Another group of fruits left without coating for comparison (control). The coated and un-coated (control) fruits were packed in carton packages and stored at room temperature (12–22 ℃) and relative humidity (RH) of 65–70%, from February to April for about 70 days.

Preparation of CMCS/PVA/Cur Membranes

The CMCS/PVA/Cur-2.5% solution as prepared previously was used for the preparation of CMCS/PVA/Cur membranes using a crosslinking agent (citric acid) and plasticizer (glycerol) [44, 48]. Briefly, 6 wt% of CMCS/PVA copolymer blend was prepared by mixing 2 wt% CMCS with 4 wt% of PVA solution with continuous stirring at 60 °C until homogeneity. Then, 2.5% of Cur-NPs (relatively to CMCS content) dissolved in 5 mL ethanol/water solution was added to CMCS/PVA mixture solution under stirring until homogeneity, followed by adding 0.5% w/w glutaraldehyde (crosslinker) and 1% w/w glycerol (compatibilizing agent and plasticizer). After complete mixing, the reaction mixture solution was kept in a water bath at 60 °C for 2 h with continuous stirring. Subsequently, the CMCS/PVA/Cur reaction mixture solution was cast in Petri dishes, followed by thermal curing in an oven at 40 °C until complete dryness. Finally, the dried CMCS/PVA/Cur membranes were exposed to gamma irradiation at different doses of 5, 10, 15, 20, and 25 kGy for further investigations and possible use in packaging applications.

Characterization of CMCS/PVA/Cur Membranes

Gel Content

A known weight of dried CMCS/PVA/Cur membranes was immersed in distilled water for 24 h and then, reweighed after removing the excess water with filter paper. The gel content percentage was determined using Eq. (1):

$$\text{Gel content}(\%) = \frac{W_d}{W_o} \times 100 \quad (1)$$

where W_d and W_o are the weight of the dried membranes after and before swelling in hot water, respectively.

Equilibrium Swelling Degree (ES)

Pieces of CMCS/PVA/Cur membranes of known weights and the known dimension of 20 mm × 20 mm were immersed in distilled water for 24 h. Then the swollen samples were re-weighed and the equilibrium swelling degree (ES) was calculated using Eq. (2):

$$\text{ES}(\%) = \frac{W_s - W_o}{W_o} \times 100 \quad (2)$$

where W_s and W_o are the weight of swollen and dried samples, respectively.

Investigation of the Quality Parameters of Sweet Orange "Valencia"

Decay (%)

Decay percentage was determined as a percentage of rotted and dry spotted peel fruits during storage (12–22 ℃ and 65–70% RH) for 70 days [30, 49].

Weight Loss (WL %)

Differences between the initial weight of nine oranges for all treatments at zero time and the weight of the same fruits at time intervals were recorded weekly by an electronic balance with a sensitivity of about 0.01 g [49–52]. The weight loss (%) for each group was calculated using Eq. (3):

$$\text{WL}(\%) = \frac{\textit{initial weight} - \textit{final weight}}{\textit{initial weight}} \times 100 \quad (3)$$

Juiciness (mL/Fruit)

The fruit juice from nine oranges of each group was extracted every week with a manual juicer during storage (12–22 ℃ and 65–70% RH); fruits were cut in half using a sharp knife after washing with tap water, then the juice was extracted and transferred to a 200 mL cylinder to estimate the volume of juice [50, 51].

Total Soluble Solids (TSS)

A drop of juice from each group was placed in a manual refractometer (0–30 Brix % mass sucrose, ATC) and the reading was recorded as a brix at room temperature [49–51, 53, 54].

pH Measurment

The acidity in Valencia orange juice of each group was determined using a digital pH meter Beekman model with a combination electrode at room temperature [49–51, 53]

Titratable Acidity (TA)

TA was estimated by titrating 10 mL of juice of each group with 0.1 sodium hydroxide using 2 drops of phenolphthalein as an indicator until the light pink color appears. The results of TA were expressed as a percentage of citric acid [49, 51, 53, 54].

TSS /TA Ratio

TSS/TA ratios of the fruit samples were calculated from the data of TSS and TA of each group by dividing TSS values by TA values [51–55].

Vitamin C (Ascorbic Acid mL/ 100 mL)

Determination of ascorbic acid was carried out according to the official method of analysis of the Association of Official Analytical Chemists (AOAC, 1990([49, 50, 53, 55]. 5 mL of juice mixed with 5 mL of acetic acid (3%) then titrate by the self-indicator dye 2,6-di-chlorophenol indophenol up to color change to sustainable pink. The strength of the dye was determined by using a standard solution of ascorbic acid, which was 0.02 mg. The ascorbic acid concentration in fruit juice is calculated by the following Eq. (4):

$$\text{Ascorbic acid (mL/100mL)} = \frac{\text{volume of dye used to titrate the juice} \times \text{dye strength (0.02)}}{\textit{sample size}} \quad (4)$$

Antimicrobial Activity

The antimicrobial activity of CMCS/PVA, CMCS/PVA/Cur-2.5%, and CMCS/PVA/Cur-10% solutions were determined by using agar or disc diffusion method and expressed as inhibition zone (mm) as previously outlined in details [24]. The antimicrobial activity was evaluated against two types of bacteria; Gram-positive such as *Bacillus Subtilis (B.S.)* (ATCC 6633) *and Staphylococcus aureus (S. aureus)*) and Gram-negative bacteria such as *Escherichia coli (E. coli)* (ATCC 8739) *and Klebsiella pneumoniae* (ATCC 13,883), and two types of fungi *Candida albicans (C. albicans)(ATCC 10,221)* and *Aspergillus niger (A. niger)(ATCC 16,888)*. Gentamycin and Fluconazole were used as a positive control for bacteria and fungi, respectively.

Determination of CMCS/PVA/Cur-2.5% Cytotoxicity (MTT Protocol)

The effect of the coating solution was examined by viability/cytotoxicity test. The MTT protocol was assayed according to the method described previously [57, 58] as follows: the 96 well tissue culture plate was inoculated with 1×10^5 cells/ mL (100 µL/well) and incubated at 37 °C for 24 h to develop a complete monolayer sheet. The growth medium was decanted from 96 well micro titer plates after a confluent sheet of cells was formed, and the cell monolayer was washed twice with wash media. A two-fold dilution of the tested sample was made in RPMI medium with 2% serum (maintenance medium). 0.1 mL of each dilution was tested in different wells leaving 3 wells as control, receiving only maintenance medium. Plate was incubated at 37 °C and examined. Cells were checked for any physical signs of toxicity, e.g. partial or complete loss of the monolayer, rounding, shrinkage, or cell granulation. MTT solution was prepared (5 mg/mL in PBS) (BIO BASIC CANADA INC). 20 µL MTT solution was added to each well. Place on a shaking table, 150 rpm for 5 min, to thoroughly mix the MTT into the media. Incubate (37C, 5% CO_2) for 4 h to allow the MTT to be metabolized. Dump off the media. (dry plate on paper towels to remove residue if necessary. Resuspend formazan (MTT metabolic product) in 200 µL DMSO. Place on a shaking table, 150 rpm for 5 min, to thoroughly mix the formazan into the solvent. Read optical density at 560 nm and subtract background at 620 nm. Optical density should be directly correlated with cell quantity.

Physicochemical Characterization

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, Bruker Optik GmbH was used to investigate the structure of prepared samples Ettlingen, Germany. X-ray diffraction (XRD) analysis was made by XRD-6000 series using Ni-filter and Cu-Kα radiation target (λ = 1.54056 A) of Shimadzu Scientific Instruments (SSI), Kyoto, Japan. The tensile strength and elongation at break (%) were measured using dumbbell-shaped pieces 50 mm long and 4 mm neck width at a crosshead speed of 500 mm/min at room temperature with a tension speed of 25 mm/min, using a tensile testing machine Qchida computerized testing

machine, Dongguan Haida Equipment Co. Ltd. China. The particle size of Cur-NPs was estimated by dynamic light scattering (DLS-ZP/Particle Sizer NICOMP 380ZLS), USA. For DLS measurement, 0.01 g of Cur-NPs was dispersed in 10 ml distilled water, stirred in an ultrasonic water bath for 30 min, and then the supernatant was used for subsequent measurements. Transmission Electron Microscopy (TEM), JEOL JSM–100 CX, Japan, with an acceleration voltage of 80 kV was used to study the particle size and distribution of Cur-NPs. For TEM measurement, the sample was prepared by distributing Cur-NPs in acetone using an ultrasonic water bath. Then, a drop of the suspension (10 µL) was dropped into the carbon-coated copper grid and left to dry at room temperature for further investigation. The wavelength of Cur-NPs was monitored by UV–Vis spectroscopy (UV-1200 spectrophotometer, Shanghai Mapada Instruments Co., Ltd., China). The Scanning electron microscopy (SEM) SEM of ZEISS EVO 15 SEM, UK was used to investigate surface morphology after being sputter-coated with gold for 3 min.

Experimental Design and Statistical Analysis

The design of the experiment was completely randomized with three replicates. The data were analyzed using the analysis of variance technique (tow way ANOVA) to compare the average value of the parameters. Duncan's multiple range test (DMRT) was used to compare the mean values between pairs of treatments [59].

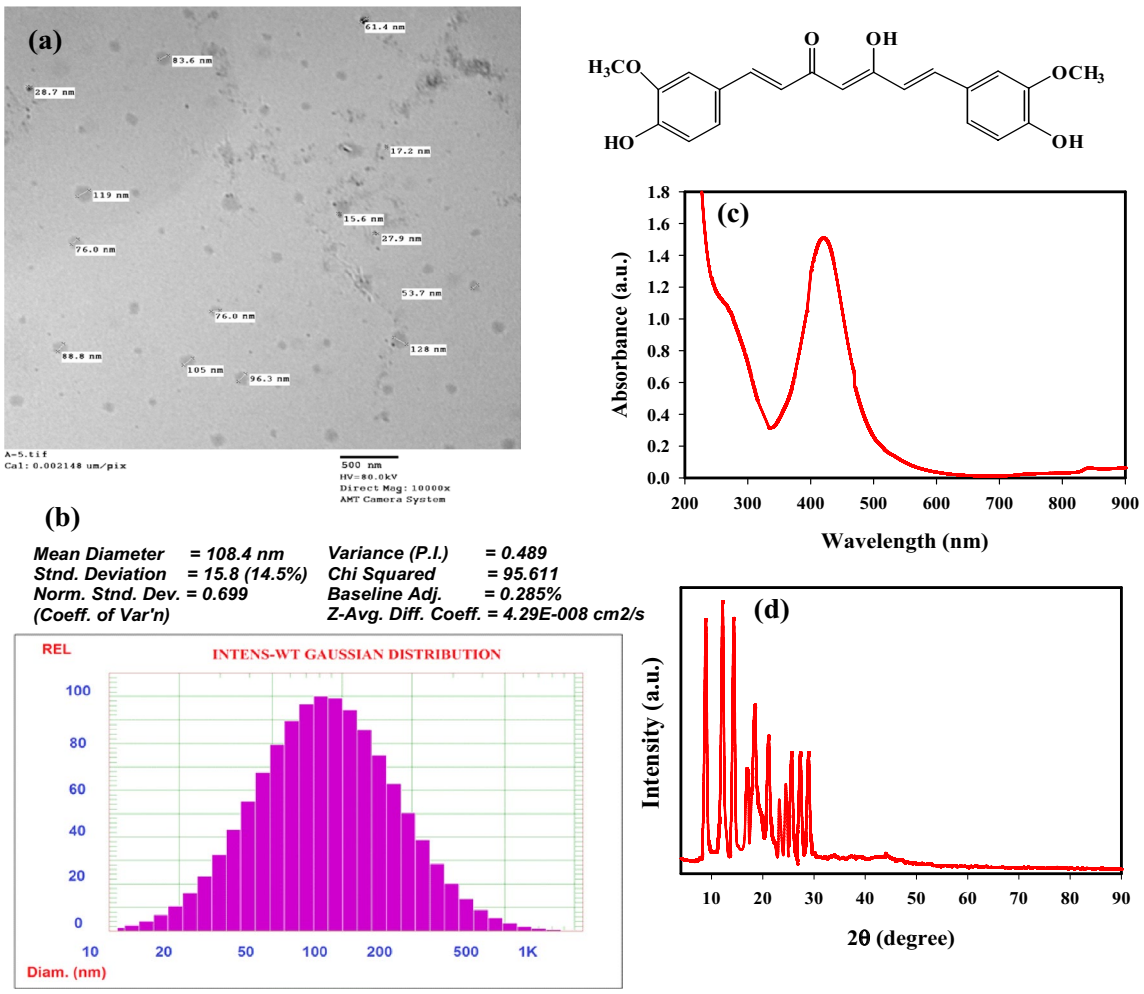

Fig. 1 The structure and characterization of Cur-NPs using **a** TEM, **b** DLS, **c** UV–Vis spectroscopy, and **d** XRD analysis

Results and Discussion

Characterization of Cur-NPs

Figure 1 describes the structure and characterization analysis of the prepared Cur-NPs using different techniques such as TEM, DLS, UV–vis spectroscopy, and XRD. Figure 1a shows the TEM micrograph of Cur-NPs. Cur-NPs nanoparticles appeared uniform and spherical particle shape and well without aggregates with an average size of 76 nm. The small particle size of the prepared Cur-NPs has shown improvement in its efficacy, solubility, and bioavailability [60]. Figure 1b represents particle size and distribution of Cur-NPs using DLS particle size analyzer. The results displayed that Cur-NPs exhibited a narrow size and enhanced distribution of an average size of 108 nm, which is nearly large than that obtained from TEM due to the association and aggregation molecules of nanocomposite in aqueous media via Vander Waal's force or hydrogen bonding.

The UV–visible spectrum of Cur-NPs is shown in Fig. 1c. The maximum wavelength (λ_{max}) of Cur-NPs was found at 418 nm which is the characteristic absorption peak of Cur-NPs. It was reported that the λ_{max} of native curcumin was 450 nm [20] and the optical wavelength of curcumin is influenced by the crystal size. The shift of the UV–visible peak to a lower wavelength is due to size reduction. Therefore, the decrease in λ_{max} exhibited a blue shift and this may be due to the reduction in its size and formation of Cur-NPs. Accordingly, the decrease in size enhances solubility and bioavailability. The solubility of Cur-NPs was estimated in water compared to the native curcumin. It is well known that curcumin is insoluble in water, which is due to the existence of insoluble flakes. However, the prepared Cur-NPs were very fine powder and readily dispersed and soluble in water and in an aqueous medium in addition they possessed good stability without aggregation. The enhanced solubility of Cur-NPs could be ascribed to their larger surface area, which promotes dissolution property [61, 62].

Figure 1d illustrates the XRD curve of Cur-NPs. It exhibited a mainly amorphous character with the typical peaks at 2θ = 8.8°, 12.1°, 14.3°, 17.2°, 18.0°, 21.0°, 23.1°, 24.4°, 25.5°, 27.2°, and 28.8° [63]. These characteristic peaks confirm the formation of Cur-NPs.

The average crystallite dimension (d) of Cur-NPs was calculated using Debeys–Scherrer Eq. (5):

$$D = \frac{k\lambda}{\beta \mathrm{Cos}\theta} \quad (5)$$

where D is particle diameter size, k is the shape or geometry factor which equals 0.9, λ is the X-ray wavelength (λ = 0.1541 nm), β is the full width at half maximum (FWHM) of diffraction peak and θ is the diffraction angle. The calculated average crystallite dimension (D) was 64.7 nm. These results confirmed that Cur-NPs possessed enhanced dissolution, small size, and good crystallinity.

FTIR Results

FT-IR spectra of CS, CMCS, PVA, Cur-NPs, and CMC/PVA/Cur membrane were presented in Fig. 2. Figure 2a shows the FTIR spectrum of CS. The typical peaks of CS were observed; including the peak at 3380 cm^{-1} is attributed to –OH and N–H groups. The peaks at 2980–2890 cm^{-1} are assigned to the asymmetric and symmetric stretching vibration of the CH_2 and CH_3 groups. Furthermore, the pending vibrations of CH_2 and CH_3 groups were also observed at 1384 and 1450 cm^{-1}, respectively. The peak at 1650 cm^{-1} is assigned to the stretching vibration of the C=O group of amide. The peak at 1598 cm^{-1} is due to the N–H bending of the NH_2 group. The peaks at 1154–1089 cm-1 are attributed to the C–O–C group of asymmetric bridge-O-stretch, skeletal vibration involving the C–O stretch, C–OH, and CH_2OH [64].

Figure 2b shows the FTIR spectrum of CMCS; a new peak at 1745 cm^{-1} due to the $–COO^-$ group [65]. The peak that appeared at 1651 cm^{-1} was shifted to 1639 cm^{-1} due

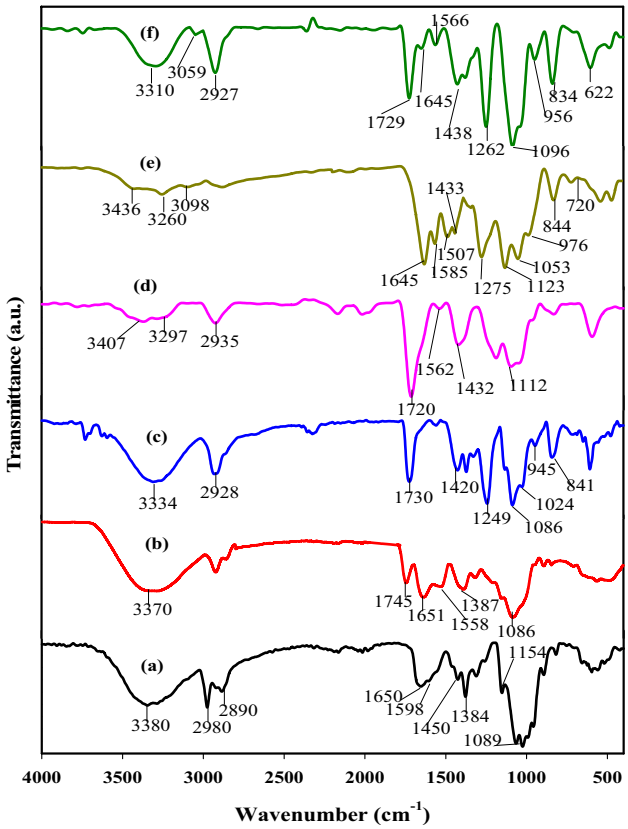

Fig. 2 FT-IR spectra of (a) CS, (b) CMCS, (c) PVA, (d) MCS/PVA membrane, (e) Cur-NPs and (f) CMCS/PVA/Cur membrane

to the carboxymethylation of CS. The peaks at 1651, 1387, and 1086 cm^{-1} became more intense than those of CS. Furthermore, the peak at 3370 cm^{-1} related to the –NH and –OH functional groups became broader and wider. These results confirm that the carboxymethylation occurred on both amino and hydroxyl sites of the glucosamine units in the CS structure [66]. Additionally, the FTIR spectrum of CMCS includes several peaks at 1558, and 1121 cm^{-1} related to C–O stretching, N–H, and C–O stretching, respectively [41, 67].

The FTIR spectrum of PVA (Fig. 2c) exhibits peaks at 3334, 2928, 1730, and 1432–1249 cm^{-1} are attributed to the –OH groups, C–H stretching vibration of $–CH_2$ groups, C=O (the remaining acetate groups in PVA) and C–O from the residual ester groups, respectively. The peaks at 1133 and 1086–1024 cm^{-1} are assigned to the peaks characteristic of C–O–C and C–O stretching vibrations, respectively. The peaks at 945—841 cm^{-1} are assigned to $–CH_2–$ group deformation [68].

Figure 2d shows the FTIR spectrum of the CMCS/PVA membrane. The peaks at 3407 and 3297 cm^{-1} are assigned to the stretching absorption bands of –OH and –NH. The peaks at 1720, 1562, and 1432 cm^{-1} which are attributed to C=O, C–O stretching, and N–H, respectively were shifted to a lower wavenumber and became wider indicating the interaction between PVA and CMCS. This is due to hydrogen bonding between –OH of PVA and C=O or –C–N– of CMCS [48]. The peak at 1112 cm^{-1} is characteristic of C–OH stretching**.** In addition to The absorption peak at 2927 cm^{-1} assigned to $–CH_2$ stretching vibration of PVA became wider and shifted to 2935 cm^{-1} after adding CMCS confirming the crosslinking between them [69].

The FTIR spectrum of Cur-NPs (Fig. 2e) exhibited characteristic peaks at 3436 and 3260 cm^{-1} that were assigned to O–H groups (phenolic O–H stretching vibration). The peak at 3098 cm^{-1} was related to C-H aromatic stretching. The peaks at 1645 cm^{-1} and 1585 cm^{-1} were assigned to the C=O and C=C vibrations in unsaturated hydrocarbons and aromatic rings, respectively. The peaks at 1433 and 1275 Cm^{-1} are related to the stretching vibration of C–O in the phenolic structure. The peak at 1507 cm^{-1} was related to C–O and C–C vibrations. The peaks at 1123 and 1053 cm^{-1} are assigned to C–O–C stretching vibrations, respectively. The peaks at 976, 834, and 720 cm^{-1} are corresponding to the stretching vibration of the $–CH_2$ group and the bending vibrations of C–H of the aromatic ring [70].

Figure 2f shows the FTIR spectrum of the CMCS/PVA/Cur membrane. After the incorporation of Cur-NPS into the CMCS/PVA matrix, various typical peaks were shifted such as the typical peaks of CMCS/PVA appeared at 1729, 1568, and 1438 cm^{-1} attributed to C=O, C–O stretching, and N–H, respectively. The peak at 3310 cm^{-1} became wide due to the stretching absorption bands of –OH and –NH of CMCS/PVA and Cur-NPs. Additionally, the intensities of some of the main peaks of Cur-NPs were noticed with some shifts and appeared with less distinct such as the peaks at 3310, 3059, 1645, 1566, and 1438 cm^{-1} which are corresponding to the stretching vibration of –OH groups, C–H aromatic stretching, C=C stretching, stretching symmetric vibrations of the (C=C) aromatic ring, and olefinic C–H bending vibrations, respectively. Additionally, the peaks assigned to enol peaks of C–O and C–O–C were observed at 1262 and 1096 cm^{-1}, respectively. Furthermore, the peaks within the region 956–622 cm^{-1} correspond to the stretching vibration of aromatic C=C of curcumin. The existence of all these peaks confirms the successful interaction between the functional groups of Cur-NPs with functional groups of CMCS and PVA [70, 71].

XRD Results

The X-ray diffraction curves of CS, CMCS, PVA, CMCS/PVA, Cur-NPs, and CMCS/PVA/Cur are presented in Fig. 3. The XRD curve of pure CS (Fig. 3a) shows two characteristics of intense crystallite peaks observed at 2θ of 10.3° and 19.5° corresponding to crystal form (I) and

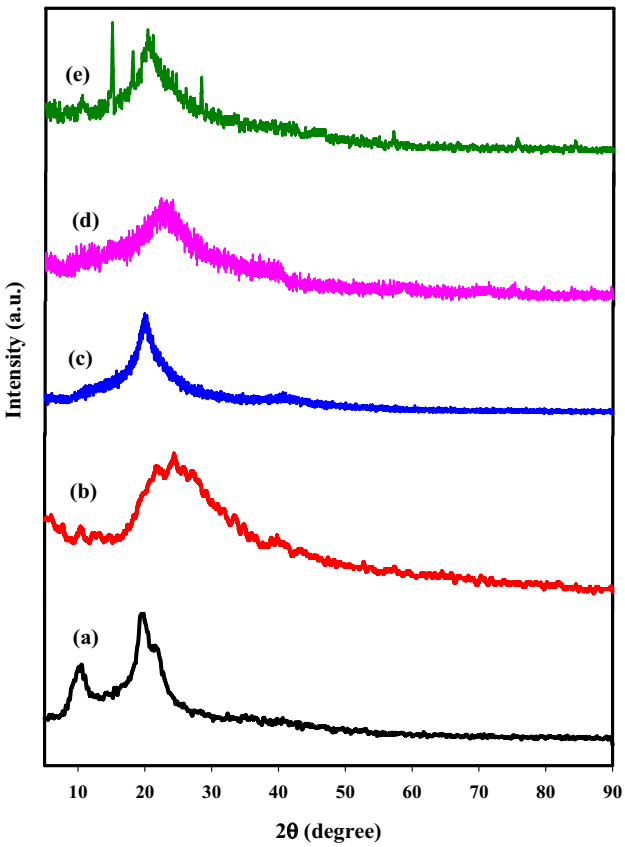

Fig. 3 XRD curves of **a** CS, **b** CMCS, **c** PVA, **d** CMCS/PVA, and (**e**) CMCS/PVA/Cur membrane

crystal form (II), indicating a high degree of crystallinity. This was due to the inter-molecular and extra-molecular hydrogen bonding between hydroxyl and amino groups [72]. After the carboxymethylation of CS, the XRD of CMCS (Fig. 3b) had a relatively broad peak at 2θ of 23.3°, and the crystalline structure was destroyed and became more amorphous. The chemical modification of CS hindered the formation of inter- and extra-molecular hydrogen bonds. Accordingly, the solubility of CSCS is better than that of CS. CMCS was soluble in distilled water up to 2.5% (w/v). The solution was transparent, pale yellow, and slightly viscous.

The main XRD diffraction peak of CMCS/PVA membrane (Fig. 3d) appears at 2θ of 22° with lower intensity than that of PVA (Fig. 3c) which appears at 2θ of 19.3° which related to the semi-crystalline nature of PVA [73]. This inferred the hydrogen bond interaction between CMCS and PVA.

The main diffraction peak of the CMCS/PVA membrane (Fig. 3d) appears at 2θ of 19° and is lowers than that of PVA due to the hydrogen bond interaction formed between PVA and CMCS. The XRD curve of CMCS/PVA/Cur membrane (Fig. 3e) confirmed the existence of crystalline diffraction peak of CMCS/PVA at 2θ of 19.4° besides the typical peaks of Cur-NPs at 2θ of 14.1° and 17.2°. Moreover, the decreasing in the number of peaks of Cur-NPs indicated that the crystallinity changed into an amorphous form as a result, there were no diffraction peaks for free Cur-NPs observed. It has been reported in earlier studies that curcumin loses its crystallinity when it incorporates with polymers [74]. This result designates that the intermolecular interactions between CMCS/PVA polymer chains offer an amorphous nature to Cur-NPs after blending.

Effect of Irradiation Dose on Gelation and Equilibrium Swelling Percentages of CMCS/PVA/Cur Membranes

Figure 4 shows the effect of irradiation doses on the equilibrium swelling and gel content percentages of the CMCS/PVA/Cur membrane. The equilibrium swelling percentage (ES %) of CMCS/PVA/Cur membrane decreases with increasing the dose as well as the existence of phenyl rings and methyl groups in curcumin contributes to their hydrophobic nature [75]. With the increase in the dose to 15, 20, and 25 kGy, the crosslinking increased, and the ES % decreased to 23.7, 19.8, and 18.6%, respectively. Furthermore, the remarkable difference in the ES % could be assigned to the varying crosslinking density as a result of the varying gel content of the prepared membranes. On the other hand, the gel content percentage increases with increasing the dose to 15 kGy of 97.4%. Higher doses do not affect significantly the gel content percentage. This is indicating the increase in the intermolecular crosslinking of the membrane components chains which resulted in the formation of crosslinked network structure. Upon crosslinking of CMCS and PVA with Cur-NPs, the prepared membranes achieved lower water uptake. The membranes with a lower swelling degree are essential in food packaging applications. Because it avoids moisture from entering the packaged food and keeps the freshness of the food product [76].

Evolution of Mechanical Properties

The mechanical properties of polymeric membranes for use in food packaging applications are important. The effect of different doses on the TS and Eb% of CMCS/PVA/Cur membranes was presented in Fig. 5. With increasing irradiation dose, the tensile strength slightly increased from 31.75 MPa

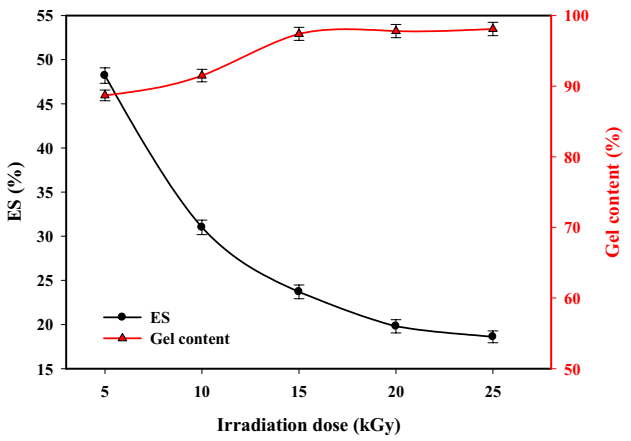

Fig. 4 Effect of irradiation dose on gel content percentage and ES of CMCS/PVA/Cur membrane

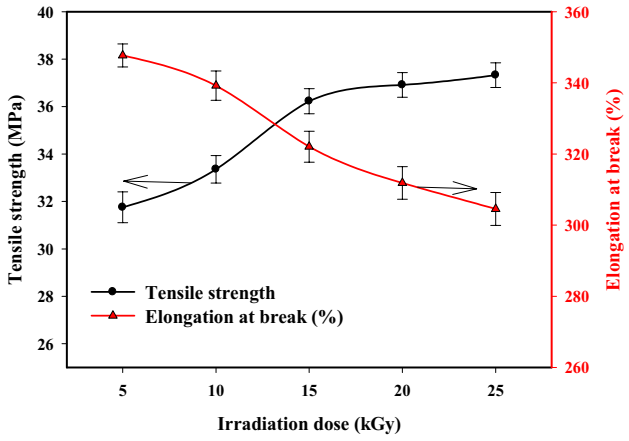

Fig. 5 Effect of irradiation dose on the tensile strength and elongation at break percentage of CMCS/PVA/Cur membranes

to 37.32 MPa. A major increase in the TS was observed at the dose of 15 kGy. This could be due to the cross-linked structure between the components of the membrane through hydrogen-bonding interactions and the interface bonding force. These interactions also simultaneously limited the movement of molecular segments. The TS value is stable with negligible values by increasing the dose up to 25 kGy. This could be attributed to the formation of crosslinking network membrane via the interaction between CMCS and PVA with Cur-NPs. Meanwhile, little decrease in the Eb% from 347 to 304%. This could be due to the increase in interfacial adhesion bonds between CMCS/PVA and Cur-NPs that forms cross-linked structure by γ-irradiation [77, 78]. As well as, crosslinking of PVA chains in the membrane with increasing the dose and the presence of a crosslinker affect the movement and flexibility of the polymer chains. It was reported that the mechanical properties of composite films are highly dependent on the interfacial interaction between the matrix and fillers [79]. The same results were observed for CUR-quaternized chitosan/PVA films [71].

Surface Morphology

The surface morphologies of the prepared CMCS/PVA and CMCS/PVA/Cur membranes were investigated by SEM as shown in Fig. 6. A smooth surface can be observed in CMCS/PVA membrane (Fig. 6a). SEM images of CMCS/PVA/Cur membranes (Fig. 6b–c) showed a homogeneous distribution of Cur-NPs on the surface of the polymer matrix of CMCS/PVA. Cur-NPs also appeared in the form of highly

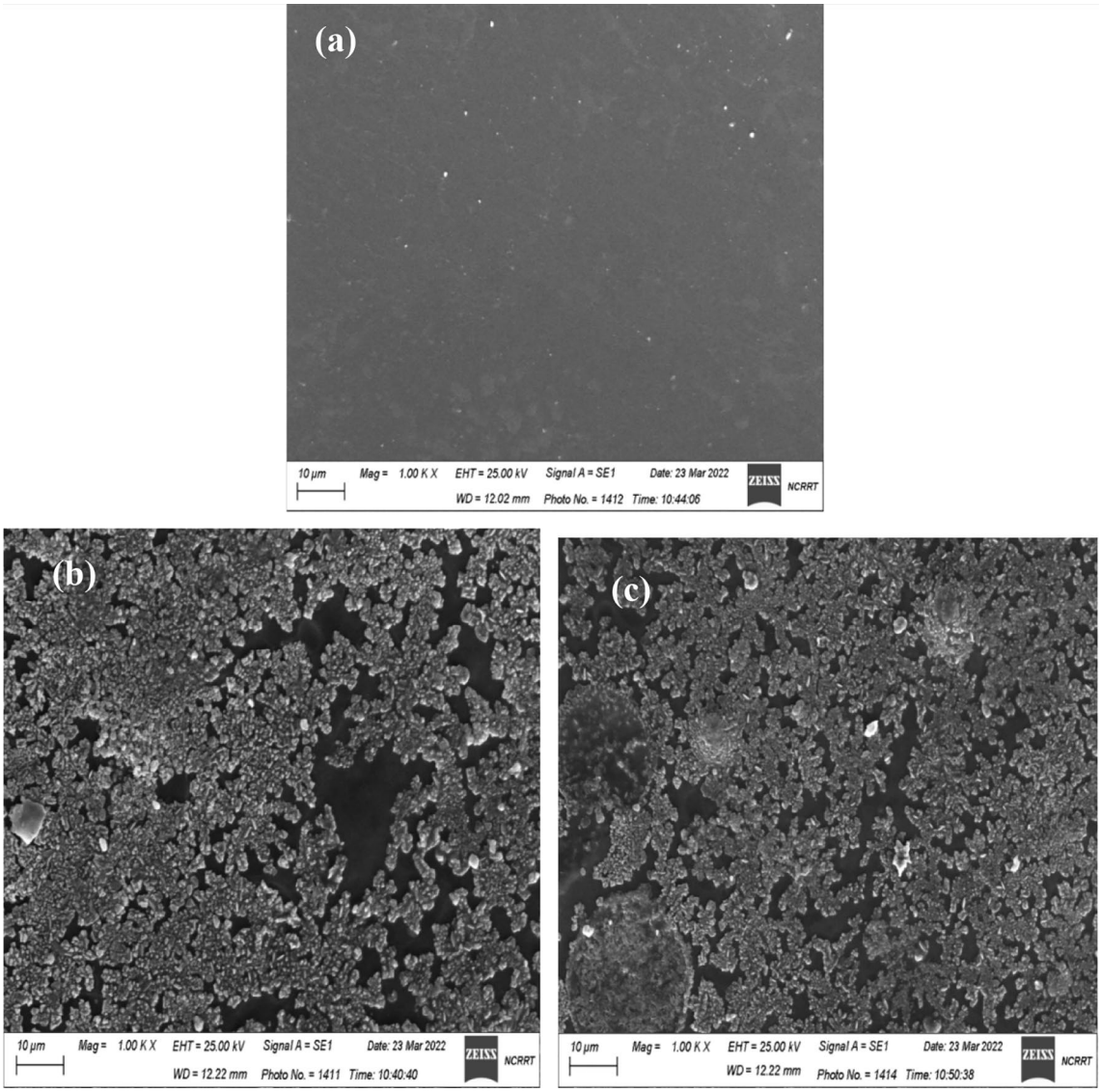

Fig. 6 SEM images of **a** CMCS/PVA membrane, **b** CMCS/PVA/Cur-2.5% membrane, and **c** CMCS/PVA/Cur-10% membrane

distributed particles and spread homogeneously within the sample with a leaf-like appearance which led to an increase in its effectiveness as a repellent for bacteria and fungi. These observations are due to the intermolecular hydrogen bonding forming tight and compressed structures. However, the highest concentration of Cur-NPs in the membrane showed a porous surface and more layered on the surface.

Eco-Friendly CMCS/PVA/Cur Edible Coating to Extend the Shelf Life of Sweet Orange "Valencia"

After treating the Valencia oranges with the prepared coating solutions CMCS/PVA/Cur of different Cur-NPs concentrations (0, 2.5, 5, and 10%), some quality parameters were assessed such as weight loss (%), decay (%) juiciness (mL/fruit), TSS., TA (citric acid %), the ratio of TSS/TA, pH, and vitamin C (ascorbic acid mL/100 mL) were assessed as follows:

Table 1 Effect of the prepared coating solutions of CMCS/PVA/Cur of different Cur-NPs ratios on the fruit decay (%) of sweet orange "Valencia" during storage at room temperature and 65–70% RH

Treatment	Fruit decay (%)				
	Number of days after coating				
	14 days	28 days	42 days	56 days	70 days
(A) control	–	–	24^{c}	36^{b}	40^{a}
(B) CMCS/PVA/Cur-2.5%	–	–	–	–	4.0^{f}
(C) CMCS/PVA/Cur-5%	–	–	–	–	7.0^{e}
(D) CMCS/PVA/Cur-10%	–	–	–	–	9.0^{d}

Means followed by the same letters are not significantly different at the 5% level

Fruit Quality (Decay %)

The decay in orange fruit owing to the metabolic activity and moisture evaporation through the surface of the flavedo layer and the infections with fungi leads to cause major economic losses by increasing shrinkage, reducing glosses, and fruits rotting. Table 1 shows the percentage of damaged fruits per 100 fruits. As it is clear, the percentage of decayed fruits was significantly higher in the uncoated fruits (control) if compared to the coated fruits. The decayed fruits included both dry, scalded, dark-colored fruits and infected with fungi as shown in Fig. 7. The results showed that the decay percentage values of fruits were affected by treatments with CMCS/PVA/Cur coating solutions significantly. The lowest percentage of fruit decay was observed for the fruits coated with the coating solution CMCS/PVA/Cur-2.5%. There was no decay percentage for coated fruits up to 56 days, whereas the decay percentage of the control sample gave 36%. At the end of the experiment, the decay percentage was 4–9% for coated fruits. The orange fruit decay percentage was almost stable in all coating treatments during a storage time of 70 days. At the end of the storage period, the lowest percentage of decay (4%) was observed in the fruits coated with CMCS/PVA/Cur-2.5% solution, while the greatest decay percentage was observed in the control (40%). It was observed that the decayed fruits of treated oranges at the end of storage included dry, shrunken, and little spotted fruits only and they were free from rotted fruits. The treatment of orange fruits

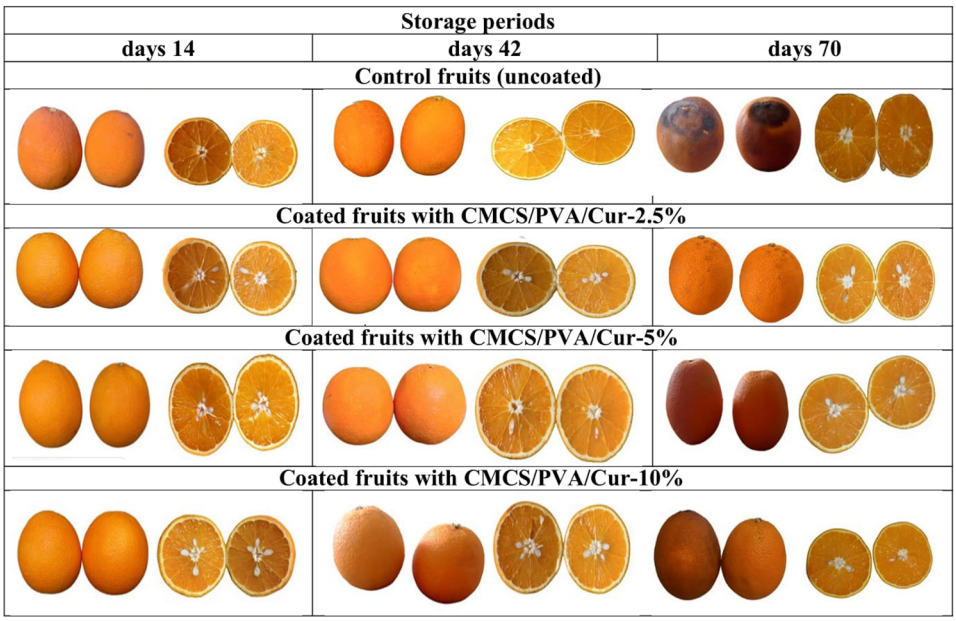

Fig. 7 Effect of CMCS/PVA/Cur coating solutions on the external quality, the internal quality, and appearance of sweet orange "Valencia" after 14, 42, and 70 days of storage at room temperature and 65–70 RH (%)

with the prepared coating solutions had a pronounced effect on the shelf life and freshness. The presence of Cur-NPs acts as smart food packaging material to prevent orange fruit contamination and ensure food quality at the same time. This is due to its antimicrobial and antioxidant properties, additionally, the presence of curcumin particles in nano size led to an increase in the efficiency of these properties [14, 80].

The effect of three coatings CMCS/PVA/Cur-2.5%, CMCS/PVA/Cur-5%, and CMCS/PVA/Cur-10% on the external quality, internal quality, and the appearance of sweet orange "Valencia" during 14, 42, and 70 days of storage at room temperature and 65–70 RH (%) compared with control samples were presented in Fig. 7. The decayed fruits included dry, scalded, dark-colored fruits and infected with fungi as shown in Fig. 7. The control fruits turned dark and lost their freshness because the peels dried out significantly due to the low humidity (65–70%) around the fruits and some brown burns appeared on the external shell of the fruits after 70 days of storage. Furthermore, shrinkage and cracks in the albedo layer were also observed in the transverse sector for control fruits.

On the other hand, the treated fruits with prepared coating solution maintained the bright color and preserved the morphological and anatomical quality of the coated oranges within an acceptable degree of quality after 70 days of storage. Furthermore, the peels of the fruits retained an acceptable degree of tenderness and a lesser degree of cracks in the albedo layer. The decay percentage of coated fruits was lower than the uncoated fruits and the color of the fruits stayed bright until the end of 70 days of storage especially the fruits coated with CMCS/PVA/Cur-2.5%. This is attributed to the antioxidant properties of Cur-NPs which preserved the bright color of the fruits [14, 80], in addition to CMCS and PVA used in coating solution acting as an active semi-permeable barrier to respiratory gases (O_2 and CO_2) between the fruit and the surrounding atmosphere, which delays the senescence and fruit decay [13, 49, 51, 81].

Weight Loss Percentage, pH, Vitamin C, and Juice Yield

The weight loss percentage, Juice yield (mL/ fruit), pH, and Vitamin C (ascorbic acid mg/100 mL) of fruits coated were presented in Fig. 8. The effect of the prepared coating solutions of CMCS/PVA/Cur of different Cur-NPs ratios on the weight loss percentage of sweet orange "Valencia" during storage at room temperature and 65–70% RH was shown in Fig. 8a. The weight loss of fruits was affected by both types of coating treatment solution and storage time. The weight loss percentage increased gradually during the storage period with increasing the days of storage, in coated and uncoated fruits. The weight loss percentage of uncoated fruits (control) was the highest until the end of 70 days. This is due to the metabolic activity and moisture evaporation through the skin (flavedo layer) and respiration rate [49, 51]. In comparison with coated fruits by the coating solutions of different ratios of Cur-NPs, the lowest weight loss percentage was observed in the fruits coated with the solution containing 2.5% of Cur-NPs, while, there was no significant difference between the fruits coated with the solution of 5% and 10% of Cur-NPs content. This is because a low concentration of Cur-NPs is sufficient in closing the stomata in the flavedo layer and reducing the respiratory rate. In addition, the layer of CMCS/PVA dried around the fruits acts as an effective semi-permeable barrier against respiratory gases (O_2 and CO_2) which delays the water loss respiration and senescence [49, 51, 82].

The effect of CMCS/PVA/Cur coating solutions of different Cur-NPs ratios on the pH of sweet orange "Valencia" during storage was shown in Fig. 8b. The results showed that the pH value of fruit juice was affected by the type of coating solution treatments and storage time. The juice pH of control fruits at zero time of storage was 3.58 and then increased with increasing the storage time up to 70 days to 4.25. On the other hand, the pH values of the coated fruits were lower than that of the uncoated fruits, but not significantly. At the end of the storage period (70 days), the pH was 4.02. A similar trend was found by many researchers when studying the effect of some edible coatings on the quality of sweet oranges [49, 51, 53, 83, 84]. They concluded that the pH value depends on the type of coating which affect the metabolic activity rate of respiration in the fruit [51].

The evolution of the change in vitamin C content (ascorbic acid mg/100 mL) in fruit through storage time is an important parameter because citrus fruits are one of the largest sources of vitamin C. The effect of CMCS/PVA/Cur coating solutions of different Cur-NPs ratios on the vitamin C content of sweet orange "Valencia" during 70 days of storage was shown in Fig. 8c. It was noticed that there were no significant changes in vitamin C content in the fruits coated by CMCS/PVA/Cur-2.5% solution during the storage period it seems stable value between 45.3–45.2 mL/100 mL from the zero time to the end of the storage period respectively. However, the changes in vitamin C content levels in control fruits decreased significantly at the end of the storage period to 44.8 mL/100 mL. This reduction is due to spontaneous oxidation by the ascorbate oxidase enzyme [83]. During 70 days of storage, the evaporation rate increased from the peel layer (flavedo), and thus the albedo layer was affected and cracked as shown previously in Fig. 7 concerning the external and internal quality, which led to an increase in internal oxygen and an increase in vitamin C oxidation [49, 85]. While, the stable value of vitamin C content in the coated fruits because the coating blend act as an active semi-permeable wall to respiratory gases, reduce moisture loss, and create a modified atmosphere, which delays the senescence and decrease oxidation of vitamin C [13, 49]. Various

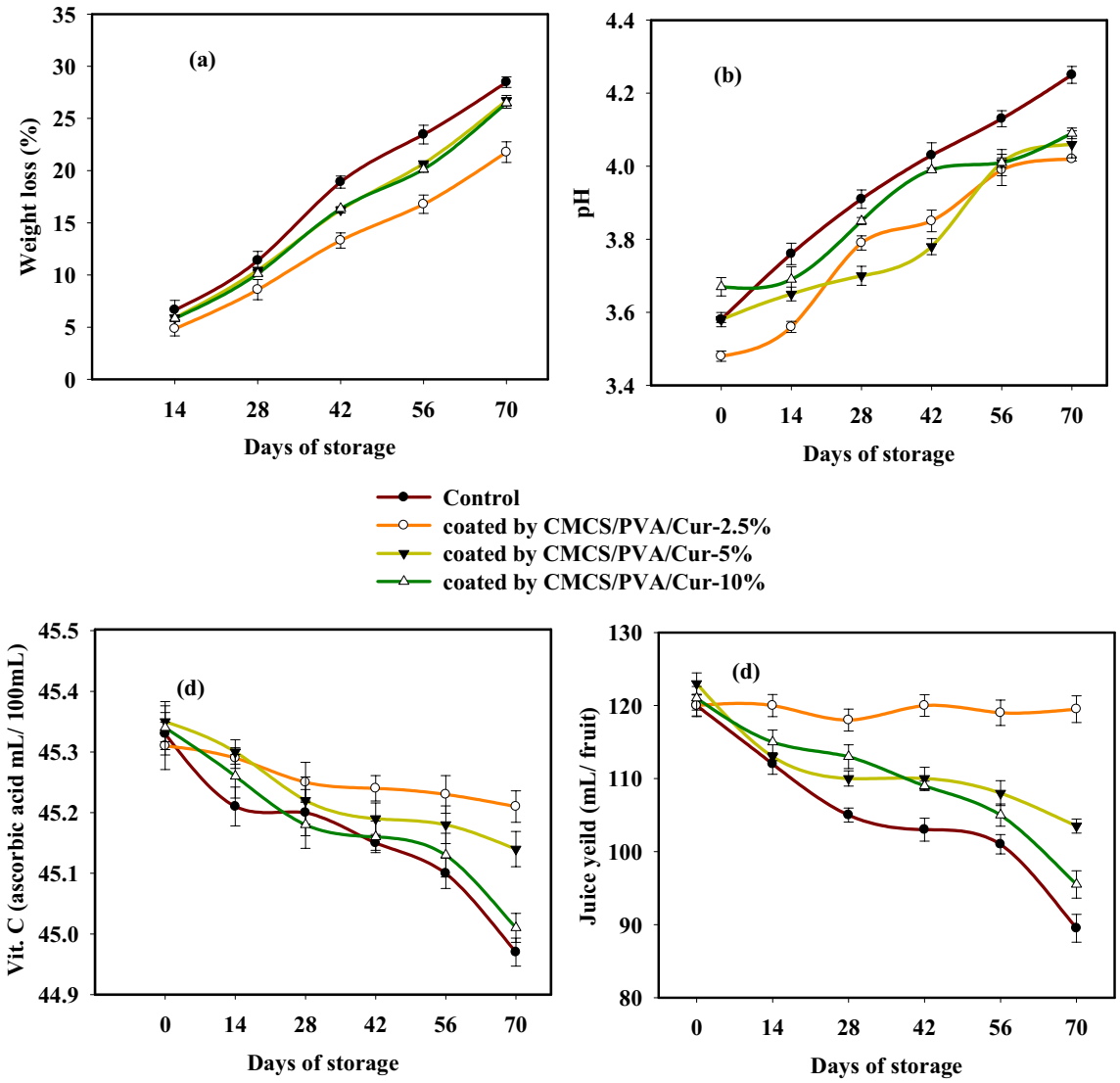

Fig. 8 Effect of CMCS/PVA/Cur coating solutions of different Cur-NPs ratios on **a** the weight loss (%), **b** pH, **c** vitamin C (ascorbic acid mL/100 mL), and **d** juiciness (mL/fruit) of sweet orange "Valencia" during storage at room temperature and 65–70% RH

reports confirmed that vitamin C loss in citrus fruits treated with edible coating techniques during storage is slightly low [84].

The effect of coating solutions of different ratios of Cur-NPs on the juice yield of sweet orange "Valencia" during storage was shown in Fig. 8d. The juice yield of fruits decreased gradually during storage at room temperature and 65–70 RH as shown in Fig. 8b. The volume of juice was another factor that was affected by treatment and storage time. The least amount of juice was in the uncoated fruits (control). While the highest amount was in the fruits coated with a concentration of 2.5% Cur-NPs. Fruit juice yield decreased significantly in all treatments during storage except the coating solution of 2.5% Cur-NPs which maintained the juice yield until the end of the storage period without significant change. The coating solution act to create a modified atmosphere that delays the senescence and preserves the softness and juiciness of the fruit tissues [49, 84]. From the all previous data, it can be noticed that the high concentration (10%) gave the opposite effect. This may be due to the accumulation of curcumin nanoparticles in high concentrations inside the pores of the peel, this led to the stress of the fruits and an increase in the aerobic or anaerobic respiration rate and the metabolic activity, or the crowding between nanoparticles did not allow free movement between the active groups, so they did not perform their role effectively. This needs to conduct more studies in the future to clarify the effect of high concentrations of nano-curcumin on the rates of ripening and respiration in fresh fruits during storage after harvest.

Total Soluble Solids (TSS), Titratable Acidity (TA), and the Ratio of TSS/TA (Maturation Index)

The effect of CMCS/PVA/Cur coating solutions of different Cur-NPs ratios on the TSS of sweet orange "Valencia" during 70 days of storage was shown in Fig. 9a. The TSS value of fruits was affected by storage time significantly. The TSS value of fruits increased gradually during the storage period. There was no significant difference in the TSS for all fruits until the 28th day of storage. Thereafter, the TSS value significantly increased in the control fruits, while an insignificant increase was observed in the coated fruits. This indicates the slow biological changes inside the coated fruits during the storage period as a result of the presence of a thin layer around the fruit that works to modify the air around it, which led to a decrease in the respiratory rate and thus delayed the senescence. Many researchers concluded that the increase in TSS value during storage could be related to the release of the soluble components which affect directly affect TSS value. This is due to the cell wall disassembly, the reduction of respiration rate, and the enhancement in dry matter due to water. In addition, the degradation of the cell wall constituents by the of effect glucosidase and galactosidase existing in citrus fruits, contributed to increasing in TSS levels [51, 86]. These outcomes are in agreement with results with other citrus fruits such as Tacle and Clara mandarin [87] and Valencia oranges [52].

The effect of CMCS/PVA/Cur coating solutions on the TA (citric acid %) of sweet orange "Valencia" was shown in Fig. 9b. It is well known that the TA of fruits decreased slightly during storage in the same mode and so the citric acid percentage decreased. The TA of all fruits decreased gradually during the storage period. While the control and the coated oranges with a high concentration of Cur-NPs (10%) were significantly less acidic than the other samples. Generally, the citric acid percentage decreases in stored citrus fruits due to the use of organic acids for energy production and alcoholic fermentation [84]. The TA of fruits was

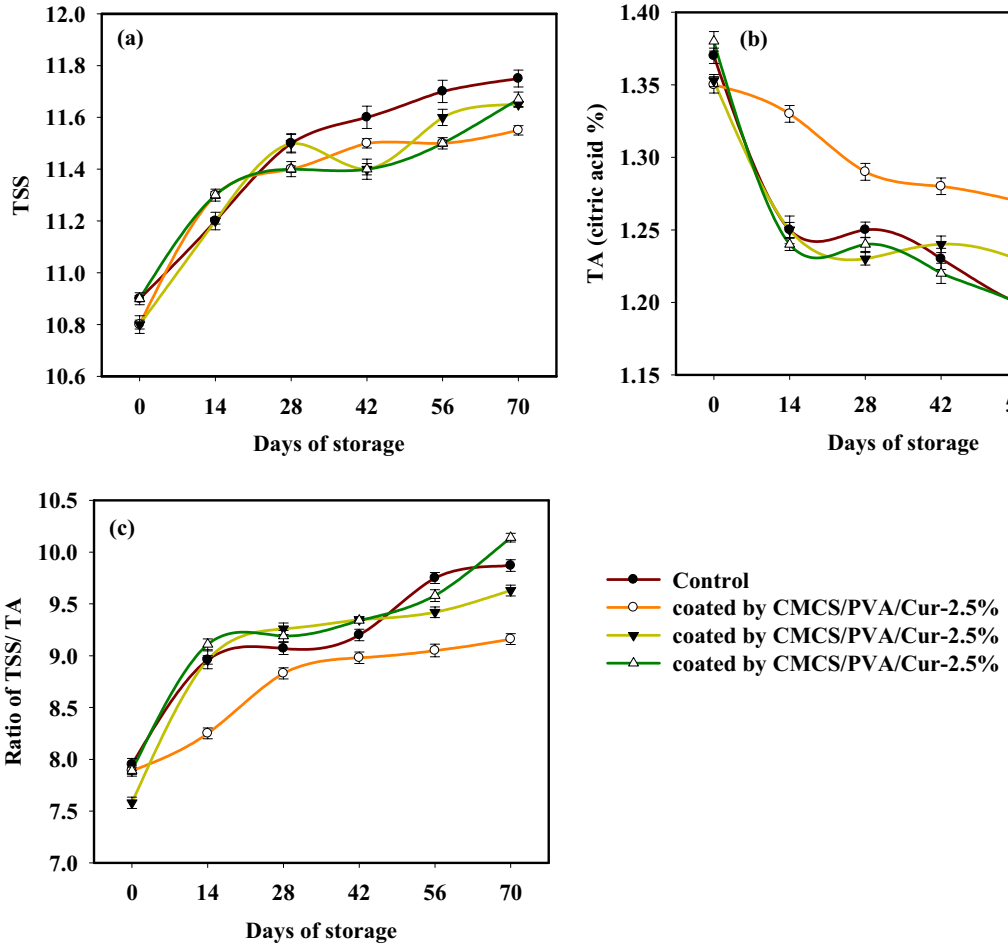

Fig. 9 Effect of CMCS/PVA/Cur coating solutions of different Cur-NPs ratios on **a** total soluble solids (TSS), **b** TA (citric acid %) and **c** TSS/TA values of sweet orange "Valencia" during storage at room temperature and 65–70% RH

1.35 at the zero time of storage and decreased insignificantly to 1.26 at the end of the storage period. The decrease in TA and acidity reduction during storage in the control fruit is due to sugar and some organic acids such as citric and malic acids are the primary substrates of respiration that affect the taste of orange fruit. The coating solutions could decrease the rate of respiration, and delay the utilization of organic acids. The coated fruits with the solution of 2.5% Cur-NPs help the fruits from TA decrease from 1.35 to 1.26 at the end of the storage experiment, thus it remained nearly constant. The coated oranges with CMCS/PVA/Cur-2.5% were higher in acidity as a result of the coating's action as a semi-permeable layer for gases and moisture, and the presence of Cur-NPs gave the coating antioxidant qualities, which led to a reduction in the respiration rate. [49, 51, 53, 84].

TSS/TA ratio is another important parameter in fruit quality and flavor that regulates consumer suitability. The TSS/TA ratio was calculated as an indicator of the fruits ripening and their rush to the senescence stage during the storage period. The increase in TSS/TA during storage is accompanied by the development of off-flavors because of the creation of ethanol in the fruit. The effect of CMCS/PVA/Cur coating solutions of different Cur-NPs ratios on the TSS/TA ratio of sweet orange "Valencia" during storage was shown in Fig. 9c. The TSS/TA ratio of fruits was also affected by both types of coating solution treatments and storage periods significantly. The TSS/TA values increased gradually with storage time. At the end of the storage period, the maturity index (TSS/TA) of control samples increased from 7.95 to 9.87. Meanwhile, the lowest value of the TSS/TA ratio of 9.16 was observed in the fruits coated by CMCS/PVA/Cur-2.5%. The treatment of fruits by the CMCS/PVA/Cur-2.5% presented promising results in maintaining the quality of the fruits for a long period (70 days) at room temperature. In contrast, the coating solution of high concentration (10%) of Cur-NPs offered the opposite effect. This may be due to the accumulation of Cur-NPs in high concentrations inside the pores of the peel, which led to the stress of the fruits and an increase in the respiration rate, or the crowding between nanoparticles did not allow free movement between the active groups, so they did not perform their role effectively. This needs to conduct more studies in the future to clarify the effect of high concentrations of Cur-NPs on the rates of ripening and respiration in fresh fruits during storage after harvest. Several studies have confirmed that the TSS percentage increases naturally, while the TA gradually decreases in orange fruits during the storage period, especially during storage at room temperature due to the increase in the respiration rate. This leads to a change in the acidic taste of the fruits and the sweet taste becomes dominant, and becomes unacceptable to the consumer [49, 51, 53, 54, 84, 88]. The results confirmed that treating the orange fruits with a coating solution of CMCS/PVA/Cur-2.5% maintained a balanced ratio between acidity and sweet taste for 70 days of storage. This was a result of the role played by coating materials in reducing the rate of respiration, oxidation, and moisture loss as mentioned previously [49, 51, 53, 84]. During the storage of orange fruits, the content of organic acids decreases faster than the content of sugars therefore, the fruits become slightly sweeter taste [89].

Antimicrobial Activity

Curcumin was discovered as a broad-spectrum antibiotic and had good antibacterial activity with a zone of inhibition against a broad range of microbes and fungi which has been proven in many studies. Figure 10 shows the antimicrobial activity of CMCS/PVA, CMCS/PVA/Cur-2.5%, and CMCS/PVA/Cur-10% solutions against two types of bacteria that can infect the Valencia oranges; *Bacillus Subtilis (B.S.)* and *Staphylococcus aureus (S. aureus)* as Gram-positive bacteria; *Escherichia coli (E. coli) and Klebsiella pneumonia (K. P.)* as Gram-negative bacteria, and two types of fungi *Candida albicans* and *Aspergillus niger*. From Fig. 10, it is clear that the CMCS/PVA without Cur-NPs showed a very limited antibacterial effect, while the minimum inhibitory zone of the prepared coating solutions CMCS/PVA/Cur-2.5% and CMCS/PVA/Cur-10% ranged from 24–27 mm which was greater than the inhibition zone of the control sample in the range of 19–25 mm. Our finding confirmed that the prepared CMCS/PVA/Cur-2.5% and CMCS/PVA/Cur-10% coating solutions had good sensitivity for both gram-positive and negative bacteria. These results were in agreement with that reported previously that curcumin extract exhibited a potent growth inhibitory effect against Gram-positive bacteria, and Gram-negative and pathogenic yeast with an inhibition zone of 9.7 mm to 10.2 mm [90]. Also, the results revealed that both CMCS/PVA/Cur-2.5% and CMCS/PVA/Cur-10% had inhibition growth of fungi of *Candida albicans* between 20–21 mm and a negative effect on *Aspergillus Niger* fungi. It is clear from the results that the presence of Cur-NPs in the coating solution has a pronouncing effect and strong antimicrobial effect because curcumin can bind to the DNA of the microbe, altering it, and thus preventing the bacterial DNA from replicating. Moreover, it damages the bacterial cell membrane and reduces the movement of microorganisms, which ultimately kills the bacterial cell [91].

Cytotoxicity

Monitoring of cytotoxicity is an important key for a material to be used in an antibacterial application in biological systems The MTT assay assisted to determine the safety profile of the prepared CMCS/PVA/Cur-2.5% coating solution. CCL-81epithelial cells were used to assess the cytotoxicity of the prepared CMCS/PVA/Cur-2.5% sample against

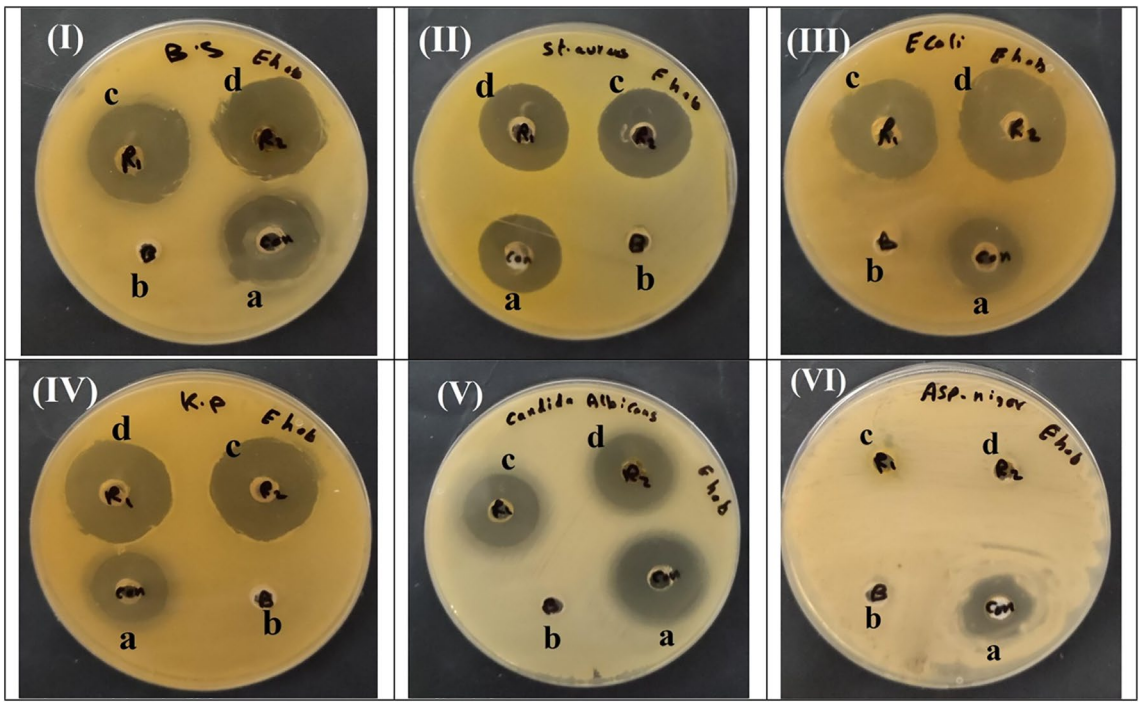

Fig. 10 Antimicrobial activity of **a** control (Gentamycin for bacteria and Fluconazole for fungi), **b** CMCS/PVA, **c** CMCS/PVA/Cur-2.5% and CMCS/PVA/Cur-10% against (I) *Bacillus Subtilis (B.S.)*, (II) *Staphylococcus aureus (S. aureus)*, (III) *Escherichia coli (E. coli)*, (IV) *Klebsiella pneumoniae (K. P.)*, (V) *Candida albicans, and* (VI) *Aspergillus Niger*

Vero cells as shown in Fig. 11 and the results were tabulated in Table 2. Cytotoxicity was qualitatively investigated using a live/dead cell viability assay and the ability of cells to proliferate within the coating solution. The results of the MTT assay indicated that cells treated with the prepared CMCS/PVA/Cur-2.5% sample exhibits non-cytotoxicity characteristics and showed high cellular viability of 98.5–99.8% of cells at all concentrations as noticed in Table 2. Additionally, the results demonstrate that the prepared coating solution had good cytocompatibility. It is apparent from this qualitative assay that CCL-81epithelial cells can grow freely on the prepared coating solution as long as the required nutrients are supplied. Based on the observed results the prepared CMCS/PVA/Cur-2.5% solution is a safe and promising material for preservation processing. Many studies have reported the dose toxicity examination of curcumin and the results revealed that curcumin is considered safe and non-toxic sign when administered up to a dose of 5000 mg/kg [92, 93].

Conclusion

The present work demonstrates the synthesis of novel CMCS/PVA/Cur coatings and membranes by gamma irradiation as packaging material to extend the shelf-life of sweet orange "Valencia" fruits. Water soluble CMCS was synthesized by carboxymethylation of chitosan and confirmed by FTIR. Extraction of curcumin from turmeric powder and converted to Cur-NPs of 76–108 nm average size was achieved by TEM and DLS analysis. The XRD results showed that Cur-NPs had good crystallinity and the calculated average crystallite dimension (D) was 64.7 nm which is in agreement with TEM and DLS results. The characteristic wavelength of Cur-NPs was at 418 nm indicated by UV-spectroscopy. Results indicated that FTIR and XRD results confirm the interaction between functional groups of Cur-NPs with CMCS/PVA polymer chains. In addition, the gel content was 97.4%, the swelling was 23.8%, and the films possessed good tensile strength at the optimum radiation dose of 15 kGy. Fruits were dipped in CMCS/PVA/Cur solutions at different concentrations of Cur-NPs (0, 2.5, 5, and 10%) and stored at room temperature of 65–70% RH for about 70 days. The efficiency of coatings was assessed by decay (%), weight loss (%), pH, vitamin C content, total soluble solids (TSS), titratable acidity (TA), and TSS/TA ratio. Quality characteristics of coated fruits were better than uncoated fruits especially the coating solution of 2.5% Cur-NPs provides accepted freshness and quality. No decay was noticed for the coated fruits till 56 days, whereas the control exhibited decay of 36%. The antimicrobial activity of CMCS/PVA/Cur-2.5% and CMCS/PVA/Cur-10% had good sensitivity for both gram-positive and negative bacteria and

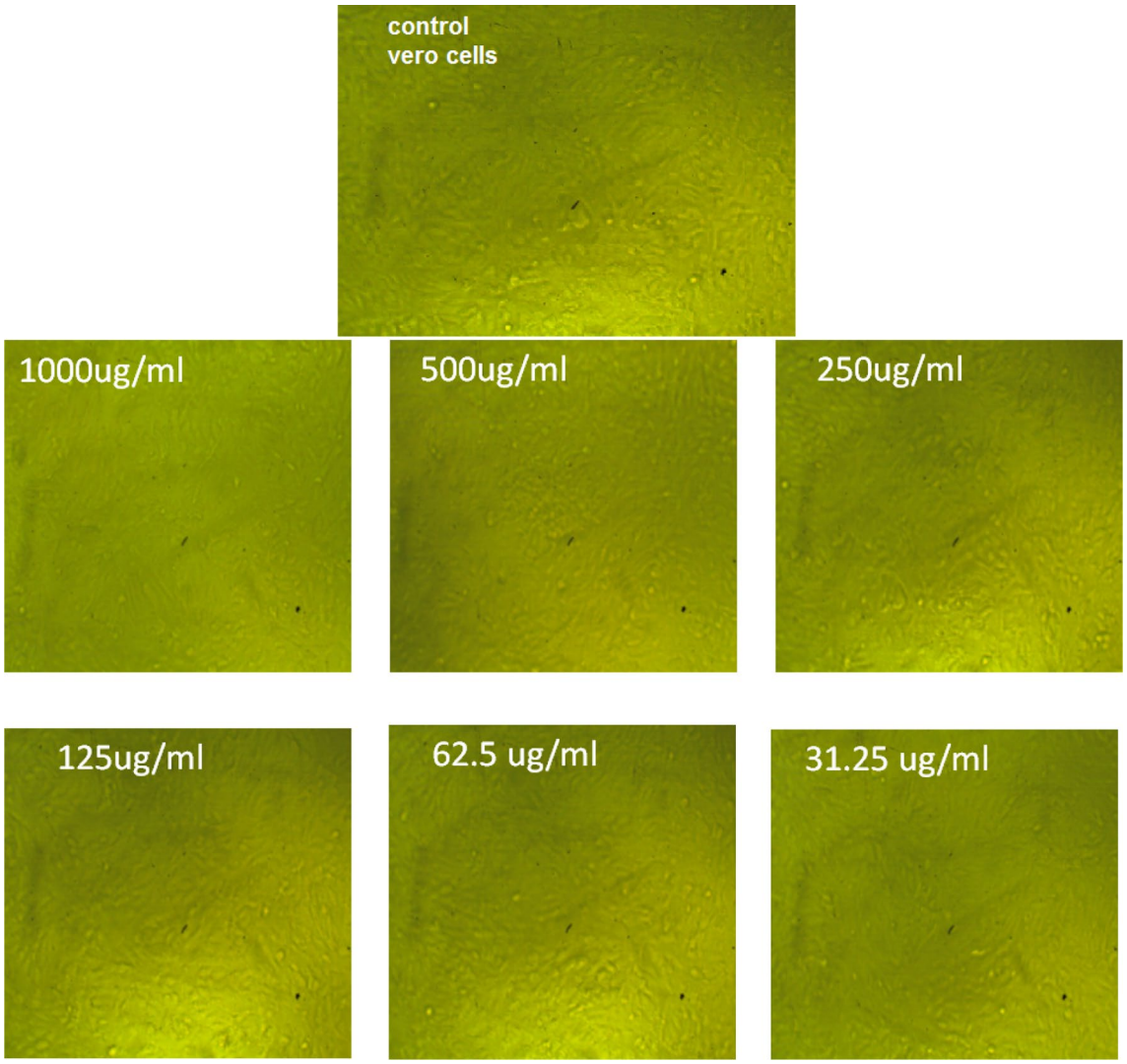

Fig. 11 The in vitro viability/cytotoxicity MTT assay of the prepared coating solution CMCS/PVA/Cur-2.5% at different concentrations against *Vero* cells

Table 2 The viability/toxicity parameters of the prepared coating solution CMCS/PVA/Cur-2.5% at different concentrations compared to *Vero* cells

ID	Conc. µg/mL	O.D			Mean O.D	±SE	Viability %	Toxicity %
Vero cells	–	0.832	0.846	0.854	0.844	0.00643	100	0
CMCS/PVA/Cur-2.5%	1000	0.821	0.845	0.83	0.832	0.00700	98.58	1.42
	500	0.833	0.839	0.846	0.839	0.00376	99.45	0.55
	250	0.84	0.847	0.837	0.842	0.00296	99.68	0.32
	125	0.844	0.841	0.84	0.842	0.00120	99.72	0.27
	62.5	0.842	0.848	0.84	0.843	0.00240	99.92	0.08
	31.25	0.846	0.836	0.845	0.842	0.00318	99.80	0.19

showed excellent inhibitory zone ranging from 24–27 mm. The cytotoxicity of the prepared CMCS/PVA/Cur-2.5% sample against Vero cells using MTT assay. It was found that the cells treated with the prepared CMCS/PVA/Cur-2.5% exhibits non-cytotoxicity characters and showed high cellular viability at all concentrations. The application of the prepared CMCS/PVA/Cur edible coating solution and films demonstrated a promising and novel packaging material to

extend the shelf life and freshness of orange fruits during storage at room temperature.

Author Contributions AME: conceptualization, methodology, investigation, validation, formal analysis, writing—original draft, writing—review & editing. EEK: investigation, validation, formal analysis, writing—original draft, writing—review & editing. AEED: methodology, investigation, validation, formal analysis, writing—original draft, writing—review & editing. NMES: validation, formal analysis, writing—review.

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Data Availability The data that support the findings are available from the corresponding author upon request.

Declarations

Conflict of interest The authors declare no competing interests.

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