

Cellulose Sulfate Active Packaging Material with Treatments on Orange Shelf Life

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Abstract: Edible cellulose sulfate (CS) was prepared by using heterogeneous process and characterized with elemental analysis, and viscosity average molecular weight. CS was evaluated as active packaging materials to keeping quality and shelf life extension of Balady orange fruits under cold storage at $5 \pm 1^\circ\text{C}$ for 45 days and additional week at $20 \pm 2^\circ\text{C}$ as a simulated marketing period. Postharvest treatments including coating and dipping by CS and CaCl_2 alone or combined was applied. Scanning electron microscopy (SEM) was used to investigate the topographic properties of peel coated surface. All treatments have a positive effect of fruit keeping quality during cold storage and extension shelf life. The best results were obtained by dipping solutions mixture with CS and CaCl_2 which achieved reducing in weight loss (83.7 %) and decay (88.5 %) as compared with the control (6.24 % and 21.67 %) respectively.

Key words: Edible Packaging Materials, Cellulose Sulfate, Calcium Chloride, Orange fruits, Cold storage, Shelf life extension.

Introduction

Packaging is extensively used for preserving, distribution, marketing fruits, vegetables, is frequently used in combination with other protection methods. However, the disposable packaging materials lead to environmental problems and further recycling expenses. Edible coating is one of the most innovative strategies to extend fruits and vegetables shelf life. Natural polymers including cellulose, proteins, and chitosan have been the significant point of growing numbers of studies reporting their prospective use as edible film or coating. There is continued upgrading of edible coating due to their great potential for food use since they can be made from a diversity of materials to control water and odor transmission and therefore improve food quality and shelf life. Edible coating can be applied to fruits to extend shelf life, protect fruits, decrease water loss, slow color change, pH and, titratable acidity during storage¹. Edible polymeric packaging materials can be fabricated from cellulose, polysaccharides, proteins and lipids. These can be made into films and can be used as wrapping materials, or films, or can be fabricated into pouches and bags for subsequent packaging use². Alginate and gellan-based edible coating films have been prepared for increasing shelf life of fresh-cut pineapples³. Retarded water loss and the decline in sensory quality, increasing the soluble solid content, titratable acidity and ascorbic acid content, retard the growth of microorganisms⁴ significantly decrease ethylene production and shelf life was extended approximately three times comparing with the control⁵. Developing edible films from biodegradable materials have been attracted worldwide attention for demand of consumers for high quality and long shelf life products and also the increased awareness of environmental issues. Edible and biodegradable natural polymer films have long been used to prohibit moisture, lipid, gas, solute, or aroma compound migration between foods and their environments as an alternative packaging's and coatings with lower environmental costs. Biopolymers commonly used in edible films are comprised edible proteincious compounds, cellulosic -based materials,

resins, lipids, and other components that render them edible⁶. Recently, Application of edible coating is a promising to improve the quality and extend shelf life of fruits and vegetables⁷. Water-soluble cellulose sulfate is the material of choice for several medical and biotechnological applications because it is biocompatible and biodegradable. Moreover, Cellulose sulfate (CS) has great potential in broad-spectrum microbicides⁸. Cellulose sulfate is the derivative of cellulose with the hydroxyl groups (OH) in cellulose substituted by sulfate groups (SO₃H) in partially or completely⁹.

One of the most important mineral elements determining fruit quality is Calcium. It is associated with many activities in the plant cell e.g., involved in protein phosphorylation via Ca-Cal modulin binding and plays a major role in senescence and ripening due to its location at cell wall and plasma membrane¹⁰. It is well known that, cell wall – bounded Ca is involved in maintaining cell wall solidity by binding carboxyl groups of polygalacturonate chains, which are mainly present in the middle lamella and primary cell wall¹¹. Postharvest Ca treatments used to increase Ca content of the cell wall which retards senescence, resulting in firmer, good quality fruit¹² with less susceptible to disease during storage^{13, 14}.

So, this study was conducted with objective to find out the new packaging suitable and alternative postharvest treatments by using cellulose sulfate as antibacterial, edible, and biodegradable coating, dipping only and or combined with calcium chloride as an innovative double to improving the storability, keeping quality and extend shelf life of Balady orange fruits

Materials and Methods

Materials

Wood pulp (α -cellulose content of 90%) was a gift from Qena of paper industry. Sulfuric acid 98% was purchased from Elnasr Company for pharmaceuticals. Anhydrous sodium sulfate and calcium chloride dihydrate were delivered from Sisco Research Laboratories PVT, LTD Mumbai. All other chemicals reagents are analytical grade.

Cellulose sulfate preparation by heterogeneous process

Cellulose sulfate sodium salt prepared by the heterogeneous process. First, cooled butyl alcohol (4°C) was dropped slowly into sulfuric acid of (- 4°C) under slight stirring to reach completely mixing, with molar ratio of sulfuric acid/butanol (1:4). And, then 1.0 g anhydrous sodium sulfate was added to reaction solution. Wood pulp was immersed in the reaction solution, which was sulfated at (- 4°C) for 3hours, and liquor ratio liquid /solid 25:1¹⁵.

Characterization

FT-IR

The cellulose sulfate sample was ground into small particles and dried under vacuum at 50 °C for 24 hours. The dried sample was analyzed in KBr discs by FT-IR (JASCO FT-IR-4100, Japan).

Elemental analysis

Sulfur content was measured with Elemental analyzer (Vario El Elementary, Germany). Total degree of substitution (DS_S) was calculated according to the equation's= (S%/32)/(C%/72)¹⁵.

X-ray diffraction: X-ray diffraction

X-ray diffraction of wood pulp and cellulose samples were carried out by PAN Alytical XPERTPR O Super X-ray diffractometer.

Viscosity Average Molecular Weight Measurements

Intrinsic viscosity measurements of the aqueous solution of cellulose sulfate sodium salt were carried out with Ubbelohde viscometer at 25±0.1°C. Molecular weight of the polymer samples can be estimated from the intrinsic viscosity $[\eta]$ values. Mark Houwink equation, $[\eta] = KM^a$ is generally employed for the estimation

of molecular weight of linear polymers where K and α values are constant for a particular polymer/solvent/temperature system¹⁶.

Scanning electron microscopy (SEM) images

Scanning electron microscope is the most widely used technique used for investigation the shape, morphology, and surface topology of films and coatings. SEM photographs of treated orange peels after cold storage were investigated under Jeol JXA-840 an Electron PROBE Microanalyzer Microscope.

Sample Storage Fruits

Balady orange fruits (*Citrus sinensis*) were obtained from a private orchard at Kaluobiya Governorate, Egypt. Fruits were picked at late April 2014 from trees grown in a loamy soil under flood irrigation system, similar in growth and received common horticulture practices. Fruits were undamaged, free from apparent pathogen infection and were uniformed in shape, and then fruits were transported to the laboratory of Agriculture Development Systems (ADS) project in the Faculty of Agriculture, Cairo University. The initial quality of the fruits after harvest was determined (in average) was as follows, fruit weight (161.7 ± 1.3 g), fruit length (7.0 ± 0.14 cm), fruit diameter (6.75 ± 0.35 cm), total soluble solids (15.8 ± 1.5 %), total acidity (1.92 ± 0.13 %) and Ascorbic acid (46 ± 2.5 mg/100ml juice).

Treatments and Storage Conditions

The selected fruits washed, air dried and placed into plastic baskets. 600 Fruits were divided into five treatments as following:

T₁: Dipping in distilled water for 2 min and kept for comparison (control).

T₂: Brush coating with Cellulose Sulfate as concentration 2% (w/v).

T₃: Dipping in 2% Cellulose sulfate solution concentration for 2 min.

T₄: Dipping in 2% CaCl₂ solution dose for 2 min.

T₅: Dipping in solution mixture of 2% (w/v) cellulose sulfate + 2% CaCl₂ in the same time.

All treatments were left to dry completely aerobically. Then, each treatment (about 120 fruits) was packed in perforated carton boxes. Six boxes as replicates were used and each box contained 20 fruits. The treated fruits inside carton boxes were stored under cold conditions at $5 \pm 1^\circ$ C and 90–95 % relative humidity (RH). Each box was divided into two sections; the first section contained 10 fruits to estimate the physical properties (percentages of weight loss and decay). The second section contained other fruits to estimate the chemical properties (fruits content of total soluble solids, total acidity and ascorbic acid). Physical and chemical measurements were recorded periodically every 15 days for 45 days.

Marketing Period

Shelflife as a simulation to marketability was examined for quality Assessments; a sample of 10 fruits of each treatment was taken out at the end of cold storage period and left at room temperature $20 \pm 2^\circ$ C up to 7 days.

Fruit Quality Assessments

Physical Characters

Weight Losses: Orange fruits were periodically weighted and the loss was recorded for each replicate. Data of weight losses were calculated as percentage from the initial weight. Decay Percentage: The number of fruits per replicate was used to express decay percentage and decayed fruits were discarded. Storage was stopped when decay assessment reached 50 % in stored fruits.

Chemical Characters

Total Soluble Solids Percentage (TSS %): measured in orange fruit juice using a T/C hand refractometer Instrument (Model 10430 Brix – readings 0 - 30 ranges Bausch & Lomb Co. Calif., USA).

Total Acidity (TA): (expressed as citric acid) and determined by titrating 5 – ml juice with 0.1N sodium hydroxide using phenolphthalein as an indicator.

Ascorbic Acid Content (VC): was determined and expressed as mg/100 ml juice by titration with 2-6 dichlorophenol indophenols blue dye.

Chemical characters including TSS%, TA and VC were determined according to standard methods¹⁷.

Statistical Analysis

The results were submitted to analysis of variance method. Differences among treatment means were determined as using the LSD test at a significance level of 0.05¹⁸.

Results and Discussions

FT-IR spectra

In this work, FT-IR spectroscopy was used to confirm the chemical structure of wood pulp and the prepared cellulose sulfate. The vibration band at 3436 cm^{-1} was attributed to OH groups of cellulose (Figure 1). The peak appears at 2916 cm^{-1} was assigned to C-H a symmetrical stretching vibration. The characteristics peak at 1639 cm^{-1} of the cellulose main structure was attributed to stretching vibration of CO group of xylan. A band appears at 1063 cm^{-1} which dominates the spectrum of cellulose linkages. Sulfate functional groups substitution was evidenced by two peaks can be seen in cellulose sulfate at 1258 cm^{-1} which corresponds to the asymmetric stretching vibration of O=S=O and 814 cm^{-1} which belong to stretching vibrations of -C-O-S confirming that product was cellulose sulfate¹⁹.

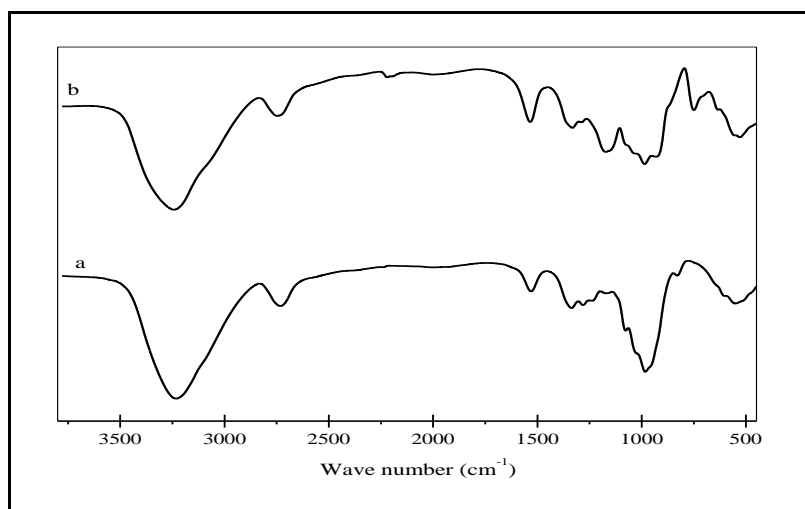


Figure 1 FT-IR spectra of (a): cellulose pulp and (b): cellulose sulfate sodium salt

The XRD patterns

In the present investigation, the X-ray diffraction was the tool by which the substitution of OH groups in the native cellulose by sulfate groups was evidenced (Figure 2). The XRD patterns of native cellulose and cellulose sulfate sodium salt were measured. The profile of native cellulose is typically cellulose XRD pattern, which exhibit high crystallinity. Two main peaks can be identified at 2θ (17°), and (22.5°) which are assigned to the (110), and (200) reflection planes. After derivatization of native cellulose by sulfation via heterogeneous process, all of the characteristic peaks disappear and a broad new one appears at approximately 2θ (10°), and (25°) is observed. This change indicates that the crystalline regions of the original native cellulose have been destroyed during dissolution and heterogeneous sulfation preparation process; so that the more stable amorphous cellulose forms are maintained^{20, 21}.

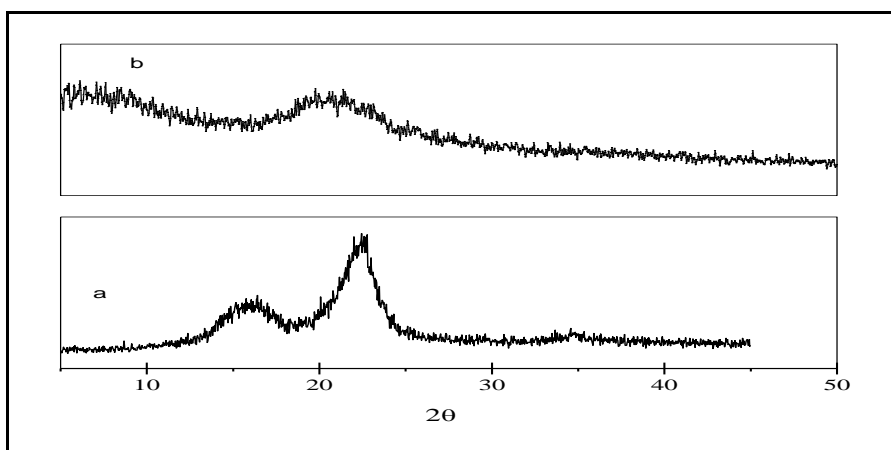


Figure 2 X-ray diffraction pattern of (a): cellulose pulp, (b): cellulose sulfate sodium salt

Total degree of substitution and molecular weight

The degree of substitution is the average number of hydroxyl group in the cellulose structure which was substituted by sulfate groups at C₂, C₃, and C₆. The results of elemental analysis of native cellulose pulp and cellulose sulfate sodium salt were determined, native cellulose pulp, C 83.76% and H 14.23%, does not show any significant presence of sulfur. In case of cellulose sulfate sodium salt, C 56.42%, S 12.28% and H 9.92%, it was found that there is considerable percentage of sulfur proving the derivatization of native cellulose on the cellulobiose units using heterogeneous sulfation process by sulfuric acid/butyl alcohol system. The total degree of substitution was 0.48.

Intrinsic viscosity, molecular weight, and degree of polymerization of water-soluble cellulose sulfate samples using concentrations 0.2-1 g/L in 6wt% NaOH solution. Intrinsic viscosity is 0.171, molecular weight 1.4×10^6 g/mole, and degree of polymerization is 7.77×10^3 .

Scanning electron microscope (SEM)

Figure 3, presents SEM microphotographs of untreated fruits peels as control (a1, a2) showed continuous, rough surface with dense distribution of zest cells pores on both upper and lower surfaces of peels. However, dipped and coated fruit peels with cellulose sulfate showed a high degree of homogeneity, dense, smooth, soft aspects, and cohesive structure with closed polymeric networks without any micro-cracks and pores which will be suggested to good barrier properties of both coating. On the other hand, dipping in calcium chloride solution gives peels of irregular, granulated peel's surface. During cold storage an increase in cell wall calcium, mainly due to the high content of calcium in the water-soluble pectin fraction, was found²². Fruit peels dipped in mixed solution CS and calcium chloride exhibited homogeneous distribution of CaCl₂ granules within cellulose sulfate as soft matrix dipping layer.

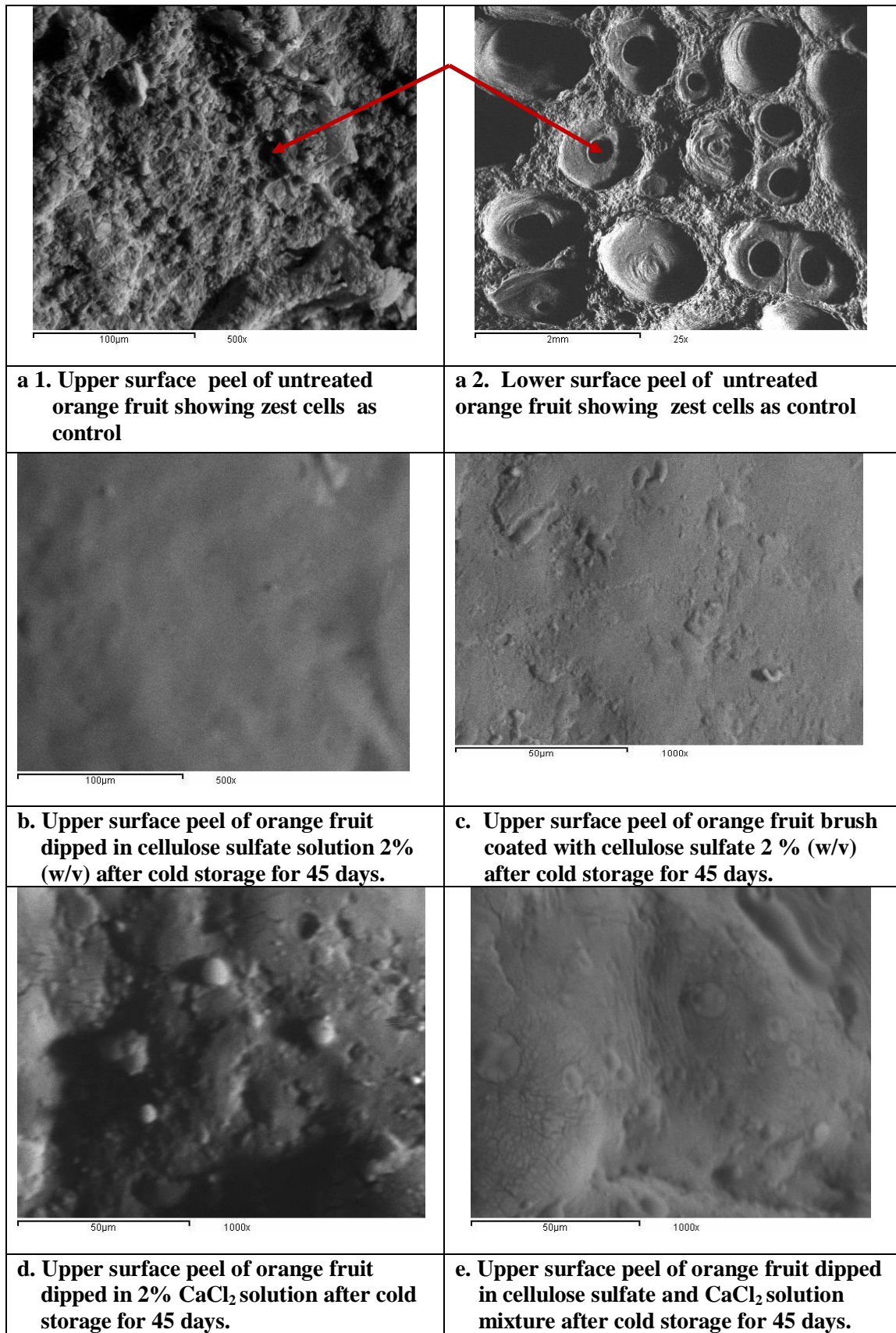


Figure 3 SEM micrographs of packaged orange fruit peels with CS and/or CaCl₂ coating

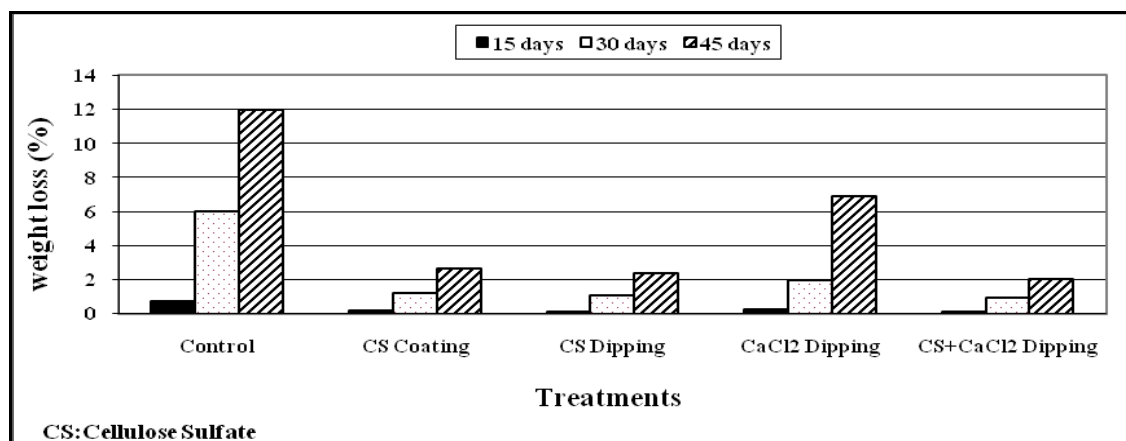


Figure 4 Fruit weight loss percentage as affect by Cellulose Sulfate and Calcium chloride postharvest treatments of Balady orange fruits stored at $5 \pm 1^{\circ}$ C for 45 days. (Means of the two seasons)

Fruit Quality Assessments after Cold Storage at $5 \pm 1^{\circ}$ C for 45 days

Regarding the effect of the different postharvest treatments on orange fruit by the periods of cold storage at $5 \pm 1^{\circ}$ C for 45 days, on weight loss %, it can be noticed that in (Figure 4), a high remarkable increasing of loss weight by the progress of storage periods. It means that weight loss was observed to increase by storage time this is may be due to the loss of water during the long periods. The main factors governing storage life of orange are water loss and susceptibility to decay. As for the comparing between the different treatments and the control on reducing weight loss by the long term of cold storage, it was observed generally that, weight loss increased through storage for untreated fruits (control) till 45days. The decline in weight loss using cellulose sulfate (CS) dipping was lower than the decline in CS brush coating. The combination dipping with T₅ was the best effect on reducing weight loss than T₃, T₂, T₄ and T₁. Otherwise, the combination dipping T₅, T₃, T₂ and T₄ recorded the lowest weight loss as compared with the control. These superiority treatments decreased the values of weight loss (%) than untreated treatment by about 83.7, 80.8, 78.7 and 51.6 % consecutively. In contrast, the highest value of weight loss was recorded with the control (6.24 %).

This result may be due to the interaction between the modes of action of Cellulose Sulfate which has compact structures after drying, there for the polysaccharide chains of CS may bind with each other during the loss of water forming a homogeneous product after drying²³. Edible chitosan coating retarded water loss and the decline in sensory quality⁴.

Using edible film or coating improves food quality and shelf life by decrease water loss during storage¹. The coatings showed good effect in keeping higher concentrations of total phenolic and anthocyanins, also maintaining lower activities of cell wall degrading enzymes²⁴. In addition, the role of CaCl₂ dipping in the physiology of plant tissue, probably to the increased resistance of tissues to the bacterial infection and action these results have an agreement with previous researcher work¹². They mentioned that postharvest Ca treatments used to increase Ca content of the cell wall which delaying senescence, resulting in firmer, higher quality fruit. Calcium infiltrations pre and postharvest in fruit tissues, delays softening rate and ripening by retarding the loss of degeneracy of cell walls. Also, coating citrus fruits is a well-known practice to improve appearance, reduce weight loss and provide a carrier for fungicides.

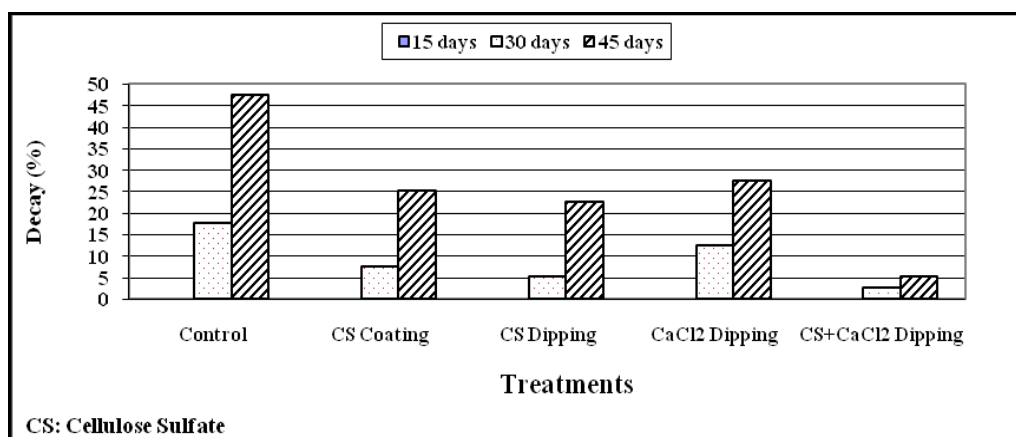


Figure 5 Fruit decay percentage as affect by Cellulose Sulfate and Calcium chloride postharvest treatments of Balady orange fruits stored at $5 \pm 1^\circ \text{C}$ for 45 days. (Means of the two seasons)

It obvious that the fruit decay % increased gradually with progression of storage period up to 45 days at $5 \pm 1^\circ \text{C}$ in a significant way. Packaging treatments developed significant effects on decay (%) of orange fruits shown in (Figure 5). Fruits CS coats, CS dips, CaCl_2 dips alone or in combined treatments was markedly produced lower decay (%) than untreated fruits. The dipping combination with T_5 , T_3 , T_2 and T_4 recorded the lowest decay as compared with T_1 . These progressed treatments decreased the values of decay (%) than untreated treatment by about 88.5, 57.7, 50.5 and 38.5 % consecutively. Conversely, the highest value of decay was recorded by the control (21.67 %).

It can be concluded that the positive effects by the dipping fruits in CS and CaCl_2 alone and/or combination during cold storage periods, it may due to the improving water holding capacity and providing a carrier for fungicides. These results agree with those obtained by⁴ who found the edible chitosan coating inhibited the growth of microorganisms. This coating, significantly reduce ethylene production and shelf life of the coated apples was extended approximately three times comparing with the control⁵. Cellulose sulfate, half ester of cellulose, exhibits a number of biological effects such as anticoagulant, antiviral, antibacterial, and antioxidant activity²⁵. Application of edible coating is pioneering to improve the quality and extend shelf life of fruits and vegetables⁷. The use of edible coating combined with natural antimicrobials is a good strategy to increase fruit shelf life²⁴. Edible and biodegradable natural polymer films have long been used to control moisture. The desired effect of calcium infiltration at 2.5% on maintaining fruit firmness may be due to the calcium association to free carboxyl group of polygalacturonate polymer stabilizing and strengthening the cell wall²⁶. It is known that calcium ions connect between peptic molecules in the middle lamella being supporting cohesion of the cell. Thus softening can be attained due to the loss of calcium from the middle-lamella and or a loss of its place in connections between the peptic molecules. The pre and post-harvest application of calcium salt has been utilized successfully in several fresh fruits to decrease loss of firmness and to slow down the ripening process. The higher water holding capacity could be related to increase firmness due to higher hardness attributes obtained with calcium treatment.

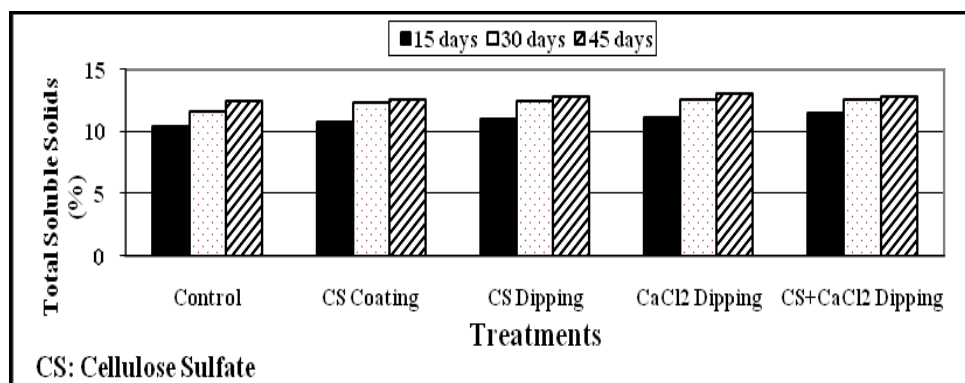


Figure 6 Total Soluble Solids (%) as affect by Cellulose Sulfate and Calcium chloride postharvest treatments of Balady orange fruits stored at $5 \pm 1^\circ \text{C}$ for 45 days. (Means of the two seasons)

As for (Figure 6) it clears that, total soluble solid percentage (TSS %) as affected by Cellulose Sulfate coating and dipping, Calcium chloride dipping alone and combined with CS as well as the control during storage $5 \pm 1^\circ \text{C}$ for 45 days, it is clearly observed that untreated and treatments postharvest orange fruits were obtained to have the higher content of TSS % by the progress the periods of cold storage after 15 days until 45 days. Generally, TSS % has an opposite pattern of the weight loss % and decay %. Concerning the effect of treatments on Balady orange fruits TSS %, although the treatments with CS dipping, CaCl_2 dipping, and CS+ CaCl_2 dipping gave the highest content of fruit TSS at the end of storage (45 days) but had no significance differences between them. While, it's gave the significant results when compared by CS coating and the control.

Our results are in line with those presented in literature⁴ who revealed that chitosan coating increasing the soluble solid content. The results are in harmony with Asymmetric previous work^{13,1}.

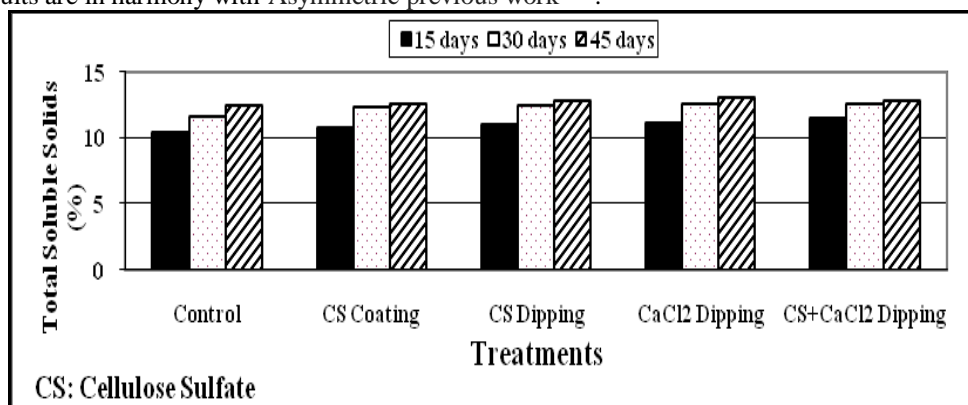


Figure 7 Total Soluble Solids (%) as affect by Cellulose Sulfate and Calcium chloride postharvest treatments of Balady orange fruits stored at $5 \pm 1^\circ \text{C}$ for 45 days.(Means of the two seasons)

Regarding the effect of the treatments on total acidity percentage (TA %) observed in (Figure 7) that postharvest treatments had the lowest (TA %) level compared with untreated fruits (control) and that is true by the progress of cold storage periods at $5 \pm 1^\circ \text{C}$ for 45 days. There were no significant differences in TA % between the treatments and was significant by the control.

The decrease in total acidity % in orange fruits during the end of cold storage (45 days) probably due to the decrease in citric acid. These results are going in line with²⁷ who reported that the retarding the papaya fruits ripening by calcium causing enzyme activity inhibition could clarify the delay in the use of organic acid in the enzymatic reactions of respiration. Also²⁸ reported that ethylene and CO_2 decrease the total acid content. On the other hand²⁹ found that fruit dipped in calcium at 2.5 and 3.5% showed higher levels of TA % than that obtained with untreated fruits. Moreover⁴ applying a chitosan increasing titratable acidity.

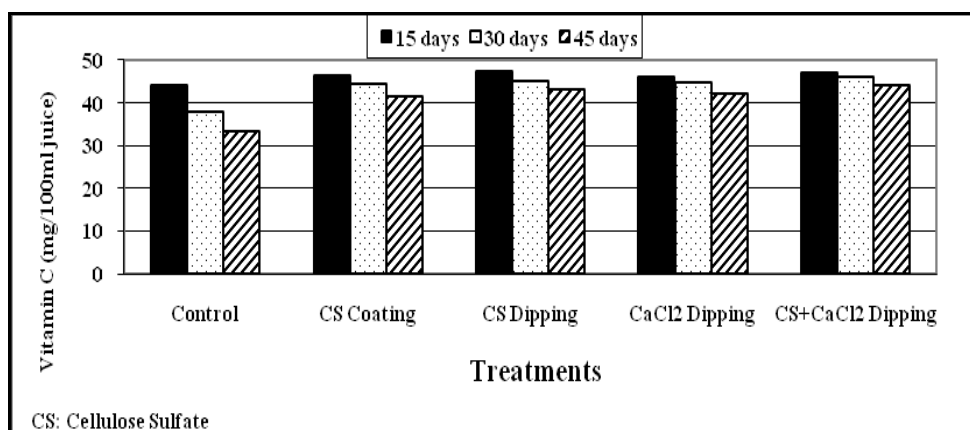


Figure 8 Vitamin C (mg/100ml juice) as affect by Cellulose Sulfate and Calcium chloride postharvest treatments of Balady orange fruits stored at $5 \pm 1^\circ \text{C}$ for 45 days. (Means of the two seasons)

Form (Figure 8) it can be noticed that Vitamin C (VC) shows a slightly reduction by the progress the storage periods of orange fruits stored at $5 \pm 1^\circ \text{C}$ for 45 days. All treatments had the highest contents of (VC) competed with untreated fruits. They did not show any significant difference between each other. Orange fruits were coating Celluloses Sulfate slightly maintained the loss of VC compared to the control treatment followed by T₄, T₃ and T₅ at the end of cold storage period (45 days).

These results are going in line with4 applying a chitosan increasing ascorbic acid content. CaCl₂ treated fruits were firmer and had more ascorbic acid than the untreated fruits and treated apple with 0-4% CaCl₂ and stored the fruit at 2°C , found that ascorbic acid content ranged between 200-400% in calcium treated fruit as compared to the control.

Fruit Quality Assessments after Marketing Period as Shelf Life

The present results in (Table 1) shows physical and chemical characteristics of Balady orange fruits stored at $5 \pm 1^\circ \text{C}$ for 45 days plus one week at room temperature ($20 \pm 1^\circ \text{C}$) as affect by cellulose sulfate and calcium chloride postharvest treatments of Balady orange fruits. It can be observed that weight loss (%), decay (%), TA (%) and VC (mg/100ml juice), had a similar pattern in all treatments. Treatments did not show significance results between each other, except the control. The combined treatment T₅ showed the best results of high quality for long shelf life. Furthermore, the combined treatment was superior to controlling weight loss (%), decay (%), TA% and V.C (mg/100ml juice), compared with control treatment after 7 days at room temperature. These results can be due to the great effect of the combination between cellulose sulfate dipping, resulted in a reduction of decay with decreased susceptibility to infection, and Calcium chloride dipping by the reduction of loss of firmness due to all wall carbohydrate metabolisms during cold storage and shelf life.

Table 1 Physical and chemical characteristics as affect by Cellulose Sulfate and Calcium Chloride postharvest treatments of Balady orange fruits stored at $5 \pm 1^\circ \text{C}$ for 45 days + 7 days at $20 \pm 2^\circ \text{C}$ (after shelf life)

Treatments	Physical and chemical characteristics					
	Weight loss (%)	Decay (%)	TSS (%)	TA (%)	VC (mg/100ml juice)	
CS coating	1.550 a	10.00 a	12.95 a	0.10 a	40.88 a	
CS dipping	0.825 a	7.50 a	12.95 a	0.08 a	42.75 a	
CaCl ₂ dipping	1.925 a	12.50 a	13.10 a	0.11 a	40.50 a	
CS+CaCl ₂ dipping	0.625 a	5.00 a	12.95 a	0.06 a	43.75 a	
Control	4.650 b	22.50 a	13.15 a	0.24 b	31.75 a	

CS: cellulose sulfate. Values with the same letter within the same column were not statistically different (Duncan Multiple at $P \leq 0.05$) (Means of the two seasons).

Calcium chloride dip treatments can maintain visual quality and firmness resulting in a longer shelf life of strawberry.³⁰ reported that calcium postharvest dip treatments at 4% and 5% respectively prolong the shelf life of mangoes under cold storage conditions without causing skin injury. Coating citrus improved appearance, reduce weight loss and provide a carrier for fungicides. Edible films form biodegradable materials demand for high quality and long shelf products¹.

Conclusions

Cellulose sulfate was successfully prepared through heterogeneous process as biodegradable natural carbohydrate coating. This investigation work has a positive effect of prolonging storage life even 45 days at $5 \pm 1^\circ \text{C}$ plus one week at room temperature ($20 \pm 2^\circ \text{C}$). The observation that, the postharvest treatments on Balady orange fruits were very benefits to storage life capacity, maintain firmness and good quality characteristics with better effects than the untreated fruits. The evaluation of their effects and optimize the best application packaging was the treatment of cellulose sulfate combined with calcium chloride dipping postharvest with had given the highest results in this respect, followed by cellulose sulfate dipping alone, CS coating and CaCl₂ dipping alone. The control treatment has the lowest ability in this respect. We have to try

many studies on the new edible packaging to keeping quality and better results in storage ability without causing toxicity on fruits.

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