Effect of natural and synthetic fruit coatings on the postharvest quality of kinnow mandarins

Muhammad A. Ali¹, Adnan Zulfiqar^{1*}, Atta M. Arif¹, Abdul-Rahim Khan¹, Zafar Iabal²and Muhammad A. Khan³

(1.Post Harvest Research Centre, Ayub Agricultural Research Institute, Faisalabad 38000, Pakistan

2. Oilseeds Research Institute, Ayub Agricultural Research Institute, Faisalabad 38000, Pakistan

3. Department of Food Engineering, Faculty of Agricultural Engineering & Technology, University of Agriculture, Faisalabad 38000,

Pakistan.)

Abstract:Natural products are more preferred by consumers now-a-days over the synthetic ones. Therefore a natural fruit coating was developed from natural ingredients (shellac, rosin, gum arabic, water and ethanol from sugar industry) without ammonia or morphine as an alternative to the synthetic coatings. So this research was devised to compare the effects of this newly developed natural fruit coating (with 9% total solids) with those of synthetic one (polyethylene based ammonia containing wax with 21% total solids) on the postharvest quality of kinnow (Citrus reticulata Blanco) mandarins. The kinnow mandarins were either coated with natural or synthetic fruit coatings or were left uncoated and stored at $5\square 2^{\circ}$ C with 8590% relative humidity for 63 days with five replications for each treatment. The results showed that both fruit coatings significantly (p<0.05) delayed changes in physiological loss in weight, firmness, ascorbic acid and overall sensory quality during the storage period as compared to uncoated fruits, while non-significant (p>0.05) changes in total soluble solids and fruit acidity were recorded for all the treatments. Furthermore the difference between natural and synthetic fruit coatings was non-significant (p>0.05). Therefore, it could be suggested that the natural fruit coating is a good alternative of the synthetic fruit coating.

Keywords: Natural fruit coating, kinnow mandarins, synthetic fruit coating, morpholine, ammonia, ethanol

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1 Introduction

Pakistan is the largest producer of kinnow (*Citrus reticulata* Blanco) mandarins (Razzaq et al., 2013) and almost 90% of the kinnow mandarin produced in Pakistan is exported (Mustafa and Ahmad, 2006). Harvested kinnows are typically brought to a packinghouse to begin the steps of preparing the fruit for market; washing, coating, grading, packing, storage and transportation (Naseer, 2010). During the washing process of fruit preparation, most of the natural wax on fruit skin is removed. It is essential that the natural waxes be replaced

by different coating materials. Various types of citrus wax formulations are available (Boonyakiat et al., 2012). Pakistan imports all of the fruit coating to apply on kinnow mandarins (PARB, 2013) which is all synthetic (mainly polyethylene based which is a petroleum by-product). But consumer trends are leaning towards more natural products, and petroleum-based waxes, such as polyethylene and paraffin, are becoming increasingly unpopular and restricted in use (Hernandez E, 1994). Edible coatings made from natural waxes, resins and polysaccharides represent an environmentally ideal package since they are biodegradable, can be consumed with the packaged product and the main ingredients are produced from renewable resources, in contrast to paraffin, mineral oil, oxidized polyethylene, and plastics, which are manufactured from a limited supply of fossil

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^{*}**Corresponding author:Adnan Zulfiqar,** Post Harvest Research Centre; Ayub Agricultural Research Institute. Email: adnanzulfiqar1036@gmail.com

fuels (Baldwin, 1994). Ammonia is also commonly used in these synthetic coatings meant for fresh fruits, but it has certain disadvantages. Ammonia-based microemulsions are difficult to prepare because ammonia is highly volatile and its vapors are unpleasant, toxic and can cause false alarms in packinghouses that use its odor as a warning that the ammonia based refrigeration system is leaking (Hagenmaier, 2004). Considering the growing interest in healthier, safer, more natural and environment-friendly products, natural coatings have been developed in recent years to avoid the use of synthetic waxes (FreshPlaza, 2013). The consumer acceptability of the coated product should have been the focus of the studies on edible coatings (Olivas et al., 2008). Reading the need of time, PostHarvest Research Centre (PHRC), Faisalabad, developed a natural fruit coating (NFC) from natural ingredients and without ammonia as an alternative to the synthetic fruit coating (based on oxidized polyethylene and containing ammonia). Therefore, the objective of current research was to compare the effects of the newly developed NFC with those of synthetic one on the post-harvest quality of kinnow (Citrus reticulata Blanco) mandarin stored at low temperature.

2 Materials and methods

2.1 Preparation of NFC

The NFC was prepared by simple atmospheric method with the following ingredients; shellac (2%), rosin (2%), gum acacia (1%), sodium hydroxide (2%), castor oil (1.5%), ethanol (26%), emulsifier Palsgaard® (0.5%) and distilled water (65%). The total solids of the final formulation were 9%. NFC was prepared in the following way; Sodium hydroxide was added to distilled water to make it alkaline. 70% of the total ethanol (26%) was also added to this alkaline water. This alkaline water was then divided into three equal parts. Shellac, rosin and gum acacia were added separately to each part of this alkaline water. After dissolving each ingredient separately, they were combined to make an alkaline mixture. Castor oil was heated to approximately $75 \,^{\circ}$ C and then emulsifier Palsgaard® was added to it. The remaining 30% ethanol of the formulation was added to the emulsified oil, which was then added to the alkaline mixture. Gentle stirring was done throughout the mixing process to ensure uniformity of the mixture. The regulatory status of different ingredients of the finalized formulation is shown in Table 1.

2.2 Choice of commercial wax

For comparison, fruit coating waterwaxFomesa (Fruitech, s.l., Valencia, Spain) was chosen amongst commercial waxes because it is widely used by the citrus industry of Pakistan and amongst its major ingredients is oxidized polyethylene (a synthetic material). The composition of Fomesa used in present study was: oxidized polyethylene wax: 10%, glycerol ester of wood rosin: 8% and ammonium hydroxide: 2% (as mentioned on label).

 Table 1Regulatory status of ingredients in the natural fruit coating (NFC).

Nome of Ingradiant	Regulatory Status						
Name of Ingredient	FDA	EU					
Castor oil	21CFR 172.876	E1503					
Rosin	21CFR 172.210	E915 ^a					
Shellac	21CFR 175.300	E904					
Gum acacia	21CFR 172.780	E414					
Ethanol	21CFR 184.1239	E1510					
Sodium Hydroxide	21CFR 184.1763	E524					

Note: FDA: Food-and-Drug-Administration; EU: European Union; CFR: Code-of-Federal-Regulation; ^aSANHA: South-African-National-Halal-Authority.

2.3 Treatment of fruit

The kinnow mandarins were grown in Chak No. 85SB, District Sargodha (Punjab, Pakistan). These were harvested with buttons in the morning, then transported in a covered vehicle to processing factory where washing was done firstly with tap water and then with the fungicidal solution of thiabendazole (Textar[®] 60-T by Tecnidex, Valencia, Spain) at the rate of 2000ppm in separate washing tanks. Subsequent drying was carried out in hot air tunnel at 50 °C for 1.50 minutes. NFC and Fomesa were applied separately to kinnow mandarins by a combination of spraying and brushing methods. The rate of coating was maintained at the rate of 1L per Tonne (1mL per Kg) of fruit because this amount of coating was officially recommended by the manufacturer (Fruitech, s. 1., Valencia, Spain) and was typical of the amount of coating widely practiced by the citrus industry of Pakistan. Additional fungicide imazalil (DECCOZIL[®]50 by Decco Italia, Italy) at the rate of 1L per 200 L of wax was added to the Fomesa wax while no additional fungicide was added to NFC at the time of application. After waxing, kinnow mandarins were dried in a hot air tunnel at 55 $\ensuremath{\mathbb{C}}$ for 1.75 minutes. After manual packing in the corrugated card boxes of 10 Kg capacity, the kinnow mandarins were pre-cooled to internal temperature of $5 \,\mathrm{C}$ by the blast air in a reefer container and then transported by the same (at 5 ± 2 °C; 85-90% relative humidity) to cold chambers of PHRC, Faisalabad and stored at 5±2 °C with 85%-90% relative humidity for 63 days.

2.4 Physical analysis

Physiological loss in weight (PLW) was determined by separately packing and tagging the samples in net bags. Individual packs of kinnow mandarins were weighed by a digital weighing balance (Sartorius GM 1501, Precision Weighing Balances, Bradford, MA, US) at the beginning of the study and thereafter weekly until the end of storage period. The result was expressed as percentage of weight loss relative to the initial weight (taken as 100%) according to the Equation 1 given below:

$$PhysiologicalLossinWeight(\%) = \frac{InitialWeight - RecordedWeight}{InitialWeight} \times 100$$
(1)

The firmness of kinnow mandarins was determined by using a digital penetrometer (model 53205, TR di Turoni, Forli, Italy) and the results were expressed as N.

2.5 Bio-chemical analysis

Total soluble solids (TSS) of kinnow mandarins were determined by using a digital refractometer (HI 96801, Hanna Instruments, Inc., Romania). Fruit acidity was determined by using digital fruit acidity meter (GMK-835F Perfect, Germany). The ascorbic acid contents of kinnow mandarins were determined according to the method as described by AOAC (2000).

The ascorbic acid contents were computed according to the Equation 2given below:

$$=\frac{1 \times R1 \times V}{R \times W \times V1} \times 100$$
 (2)

Where, R = mL of dye used in titration against 1 mL standard ascorbic acid solution (1 mg ascorbic acid /mL); R1= mL of dye used in titration against V1 mL of aliquot; V= Volume of aliquot made by 0.4% oxalic acid; W= mL sample; V1= mL aliquot taken for titration.

Samples were injected through Gas Solid Chromatography (GSC) to determine the ethanol contents according to the method described by Perez et al., (2002) described below:

Sample was prepared by extraction of kinnow mandarin juice by citrus juice reamer (Philips) in pre-sterilized 500 mL glass jars. Five mL juice was taken and transferred to 10 mL glass vials with crimp top caps and silicon septum seals for the removal of head space from the glass vials. The vials were kept at 20 °C for 1 hour, followed by 25 minutes at 30 °C to attain the equilibrium in the glass vials. Five mL head space vapors were injected into the gas chromatograph (Perkin Elmer 3920) using pointed gases tight syringe (Hamilton, USA) under following conditions:

Gas chromatograph: Perkin Elmer (3920), Perkin Elmer Life and Analytical Sciences, Wellesley, USA

Recorder:Shimadzu (C-R4A), Shimadzu Corporation, Kyoto, Japan

Column:Chromosorb glass column having 2 meters (length) x 2 mm (internal Diameter) supplied by Chromosorb, SKC, Inc., Pennsylvania, USA Column temperature: 150 °C Injector temperature: 160 °C Detector:Flame ionization detector (FID)

Detector Temperature: 250 $^{\circ}$ C

The ethanol contents were determined in all samples by the peak area comparison, retention time and peak height of the ethanol standards (99.9% Merck). The results were expressed as mg/kg.

2.6 Sensory analysis

A panel, consisting of five trained professional judges (Five replicates) of the research and development staff, from the PostHarvest Research Center, Ayub Agricultural Research Institute, Faisalabad, Pakistan, conducted the sensory analysis on weekly basis for gloss, color, flavor and overall acceptability by using 9-point hedonic scale according to the method as described by Lee et al., (2003).

2.7 Statistics

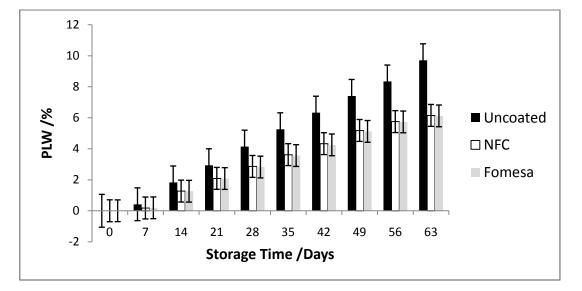
The experiment was laid out under the scheme of two-factorial completely randomized design (CRD). Five replicates were made for each treatment with five fruits per treatment. The data were subjected to analysis of variance (ANOVA) using Statistix 8.1 software and treatment means were compared using Least Significance Difference (LSD) Test at 5% level of significance ($p\leq 0.05$) (Steel et al., 1997).

3.1Physical analysis

The control of weight loss is important in that most fresh produce is sold by weight (Khout et al., 2007). Physiological loss in weight (PLW) of uncoated kinnows and the kinnows coated with the NFC and Fornesa was recorded at 9.71%, 6.15% and 6.12% respectively after 63 days of storage (Figure 1). The coated kinnows were significantly different (p<0.05) from the uncoated kinnows while those coated with the NFC and Fornesa were at statistical parity concerning the PLW. The loss of fruit weight is mainly caused by fruit transpiration in which water moves out and results in wilted rind and a shriveled appearance (Wills et al., 2007).

Water transfer is restricted by coatings that act as barriers and protect fruit skin, thus delaying dehydration (Hernandez-Munoz et al., 2008). Both coatings reduced weight loss percentage almost equally as reported earlier by Mahajan et al., (2013) who stated that wax coating successfully reduced weight loss percentage in kinnow fruits during cold storage.

Firmness of kinnows decreased gradually (Figure 2) as the storage period progressed, but the kinnows coated with the NFC retained maximum fruit firmness (Start: 17.95 N \rightarrow End: 9.91 N) followed by the kinnows coated with Fomesa (Start: 17.85 N \rightarrow End: 9.51 N) while the least firmness (Start: 17.85 N \rightarrow End: 4.80 N) was recorded for the kinnows which were uncoated.



3 Results and discussion

Figure 1 Mean values with SE for the effect of NFC and Fomesa on the physiological loss in weight (PLW) of kinnow mandarins stored at 5±2 °C, (p< 0.05)

Fruit firmness diminishes as the degree of ripening increases due to the action of pectolytic enzymes (Muramatsu et al., 1996). Coatings sustain fruit firmness by mechanisms similar to the controlled atmosphere and modified atmosphere packaging i.e., by decreasing respiration and transpiration, slowing ripening and senescence, and delaying degradation of cell wall (Bai et al., 2009; Baldwin, 1994). Similar observations were made in an earlier study on wax treated kinnow fruits by Mahajan et al., (2013).

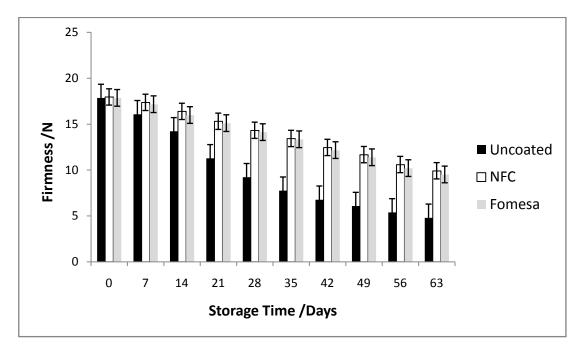


Figure 2 Mean values with SE for the effect of NFC and Fomesa on the firmness of kinnow mandarins stored at 5 ± 2 °C, (p< 0.05)

3.2Bio-chemical analysis

There was a non-significant increase in the TSS of all the treatments as the storage period progressed (Figure 3). The highest increase was observed for the uncoated kinnow mandarins (from 9.81% to 10.51%) followed by the kinnow mandarins coated with the NFC (from 9.82% to 10.41%) and Fomesa (from 9.83% to 10.42%).

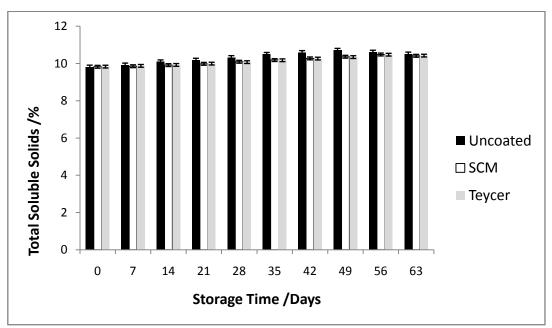


Figure 3 Mean values with SE for the effect of NFC and Fomesa on the TSS of kinnow mandarins stored at 5 ± 2 °C, (p< 0.05)

The results showed that wax coating has no significant effect on the TSS of kinnow mandarins. The slight increase in TSS of all the treatments might be due to the conversion of organic acids to sugars through gluconeogenesis (Echeverria & Ismail, 1987), and the solubilization of cell wall constituents by galactosidases and glucosidases present in citrus fruit (Burns, 1990). Similar non-significant effect of different coatings on TSS was observed in Sai Nam Pheung tangerines by Seehanam et al., (2010).

The fruit acidity continuously decreased with the increasing storage period for all the treatments (Figure 4)

but the decrease in acidity was slightly less for the coated kinnow mandarins (from 1.01% to 0.81% for NFC and from 1.03% to 0.82% for Fomesa) as compared to the uncoated ones (from 1.02% to 0.79%). The decreasing trend in the fruit acidity with the increasing storage period might be due to the oxidation of organic acid and its further utilization in metabolic processes (Obenland et al., 2011). The results of present study coincide with those of Seehanam at al., (2010) and Boonyakiat et al., (2012), who also found a non-significant decrease in the fruit acidity of waxed and unwaxed "Sai Nam Peung" tangerine fruit during storage.

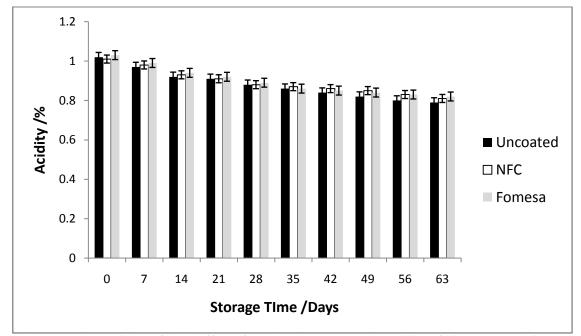


Figure 4 Mean values with SE for the effect of NFC and Fomesa on the acidity of kinnow mandarins stored at 5 ± 2 °C, (p< 0.05)

A gradual decline in the ascorbic acid contents of the kinnow mandarin was observed for all the treatments (Figure 5), but the decline was significantly less in the coated (both natural and synthetic) kinnow mandarins as compared to the uncoated ones. The maximum value was recorded for the kinnow mandarins coated with Fomesa (26.06%) followed by those coated with NFC (26.05%) while the least value was recorded for the uncoated kinnow mandarins (24.77%). Ascorbic acid is highly sensitive to oxygen and is readily oxidized when exposed to it (Hussain et al., 2006). Coatings create a modified

atmosphere and limit the exchange of gases thus reducing the amount of oxygen reaching to the interior of fruit that prevents the oxidation of ascorbic acid (Baldwin et al., 1994). These results are at par with the previous findings of studies which found that the ascorbic acid contents of waxed and unwaxed tangerines (Arekemase and Oyeyiola, 2011) and kinnow fruits (Mahajan et al., 2013) decreased during storage at low temperature and that the coated fruits had higher ascorbic acid contents than the uncoated ones (Mahajan et al., 2005). Ethanol contents exhibit great variations in citrus during storage owing to their volatile nature (Baldwin et al., 1995). The ethanol contents in kinnow mandarins increased linearly as a function of storage (Figure 6). The ethanol contents of coated and uncoated kinnow mandarins were significantly different, with higher values recorded for both of the coated kinnow mandarins as compared to the uncoated ones.

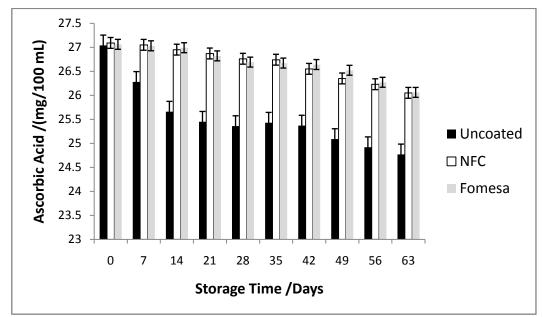


Figure 5 Mean values with SE for the effect of NFC and Fomesa on ascorbic acid contents of kinnow mandarins stored at 5 ± 2 °C, (p< 0.05)

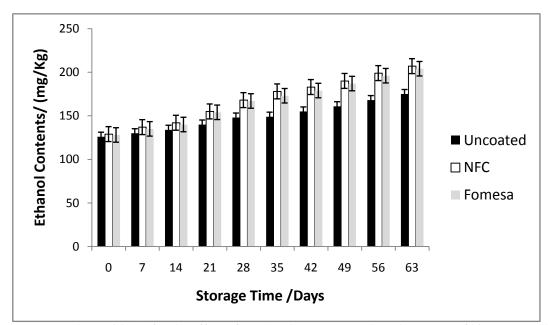


Figure 6 Mean values with SE for the effect of NFC and Fomesa on ethanol contents of kinnow mandarins stored at 5 ± 2 °C, (p< 0.05)

At start of the study, the mean values were not significantly different and ranged from 126 to 129 mg/kg for all the treatments but at the end of the study, these values were significantly different with 175 mg/kg for uncoated kinnow mandarins while 207 and 204 mg/kg for the NFC and Fomesa coated kinnow mandarins

respectively. The level of ethanol contents observed in both of the coated kinnow mandarins did not have an adverse impact on the taste/flavor of the mandarins as observed earlier by Curtis (1988) probably due to the fact that oxidized polyethylene is relatively permeable to gases (Bai and Plotto, 2011) and the permeability of shellac-type coatings increases at high humidity levels that are used for commercial citrus storage (Hagenmaier and Shaw, 1992). Furthermore, the ethanol contents of the NFC coated kinnow mandarins were not significantly different from the synthetic Fomesa coated kinnow mandarins. The higher ethanol contents for the coated kinnow mandarins might be due to the creation of a modified atmosphere created by fruit coatings that significantly affects the ethanol levels (Baldwin et al., 1995). The same increasing trend in ethanol contents was also observed by Hagenmaier (2002) for coated Valencia oranges and citrus fruits by Curtis (1988) during storage.

3.3Sensory analysis

The primary reason coatings are applied to citrus fruits is to improve appearance by imparting gloss and in that way improve marketability. Appearance can be affected by surface dehydration resulting in whitening, waxiness, and discoloration Selective coating materials can reduce moisture loss, control surface dehydration and discoloration, delay the surface whitening, and enhance the glossiness of fruit surfaces (Lin and Zhao, 2007). The kinnow mandarins coated with NFC and Fomesa showed good initial gloss as compared to the uncoated ones (Table 2) as previously reported for 'Mor' mandarins (Porat et al., 2005). The gloss provided by NFC (shellac and rosin) was slightly higher than that provided by Fomesa (polyethylene based) though it was non-significant as reported earlier by Hagenmaier and Baker (1994) that the shellac and rosin based coatings provide more gloss than coatings made from waxes such as polyethylene or carnauba wax.

The gloss decreased as the storage period progressed (Table 2) as previously observed for coated grapefruits by Arif et al., (2013). Similar pattern was observed for other sensory parameters viz. color, flavor and overall acceptability (Table 2). Hagenmaier (2002) has reported that higher rates of weight loss decrease the color scores. Both of the coatings reduced the rate of weight loss in the present study thus minimizing the negative changes on the sensory qualities. The present results are supported by the earlier findings of Seehanam et al., (2010) which said that the coated Tangerine fruits showed higher gloss and better visual appearance results as compared with the non-coated fruit. The flavor of the coated kinnow mandarins was recorded better than the uncoated ones as reported earlier by Curtis (1988), who applied a polysaccharide based fruit coating (Semperfresh) in combination with shellac to citrus fruits and recorded higher firmness, good flavor and increased ethanol levels as compared to uncoated ones.

Table 2 Means of scores for the sensory attributes for comparison of NFC and Fomesa on kinnow mandarins

stored at 5±2 °C.											
Attribute Treatment	Storage Time ,days										
	0	7	14	21	28	35	42	49	56	63	
Uncoated	7.90 ^a	7.75 ^b	7.50 ^c	7.25 ^d	7.00 ^e	6.75 ^f	6.50 ^g	6.10 ⁱ	5.75 ^j	5.25 ¹	
NFC	8.05 ^a	8.05 ^a	8.00 ^a	8.00 ^a	8.00 ^a	8.00 ^a	7.75 ^b	7.65 ^b	7.50 ^c	7.25 ^d	
Fomesa	8.00^{a}	8.00^{a}	8.00^{a}	8.00^{a}	8.00 ^a	7.95 ^a	7.75 ^b	7.60 ^b	7.50 ^c	7.25 ^d	
Uncoated	7.90 ^a	7.75 ^b	7.60 ^b	7.50 ^c	7.25 ^d	7.00 ^e	6.50 ^g	6.10 ⁱ	5.50 ^k	5.25 ¹	
NFC	8.00^{a}	8.00^{a}	8.00 ^a	8.00 ^a	8.00 ^a	7.75 ^b	7.70 ^b	7.60 ^b	7.50 ^c	7.25 ^d	
Fomesa	8.00^{a}	8.00^{a}	8.00^{a}	8.00 ^a	8.00 ^a	7.75 ^b	7.70 ^b	7.60 ^b	7.50 ^c	7.25 ^d	
Uncoated	8.00^{a}	7.90 ^a	7.80^{a}	7.75 ^b	7.50 ^c	7.25 ^d	7.00 ^e	6.50 ^g	6.25 ^h	5.50 ^k	
NFC	8.00^{a}	8.00 ^a	8.00 ^a	8.00 ^a	7.90 ^a	7.80 ^a	7.75 ^b	7.50 ^c	7.25 ^d	7.00 ^e	
Fomesa	8.00^{a}	8.00^{a}	8.00^{a}	8.00^{a}	7.90 ^a	7.80^{a}	7.75 ^b	7.55 ^b	7.25 ^d	7.00 ^e	
Uncoated	7.90 ^a	7.80 ^a	7.65 ^b	7.50 ^c	7.25 ^d	7.00 ^e	6.65 ^g	6.25 ^h	5.85 ^j	5.35 ^k	
NFC	8.00^{a}	8.00^{a}	8.00^{a}	8.00^{a}	7.95 ^a	7.85 ^a	7.75 ^b	7.60 ^b	7.40 ^c	7.15 ^d	
Fomesa	8.00^{a}	8.00^{a}	8.00^{a}	8.00^{a}	8.95 ^a	7.85 ^a	7.75 ^b	7.60 ^b	7.40 ^c	7.15 ^d	
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NFC: Natural-Fruit-Coating.

(Means in a column with different superscripts are not the same, p < 0.05, LSD)

4Conclusion

The newly developed NFC prepared by the PHRC, Ayub Agricultural Research Institute, Faisalabad proved up to the mark in efficiency. This NFC came up with non-significant differences against Fomesa in all the tested physical, bio-chemical and sensory parameters. It has an additional benefit of being the natural one and ammonia free over Fomesa which is synthetic and contains ammonia. It can safely be a good alternative of Fomesa for postharvest application on kinnow mandarins.

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