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Gases and Vapor Permeability to Carnauba and Shellac Coatings

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ABSTRACT

Study on gases and vapor permeability to carnauba and shellac using tangerines as tested fruit showed that oxygen and carbon dioxide permeated to carnauba readily. The internal gas composition as well as ethanol content of tangerine juice were only slightly altered. However, the permeability of the gases were restricted by shellac resulting in accumulation of ethanol. On the opposite, water vapor permeated to shellac better than carnauba. Shellac reduced water loss only upto 30% at 20% shellac concentration, while carnauba reduced water loss by as much as 60% at 15% carnauba concentration. The properties of mixed coating were in between the properties of each material alone. However, shellac had stronger influence than carnauba on the vapor permeability of the mixture. Study for gases and vapor permeability by coating both materials on silk-screen revealed that permeability depended also on the adhesion of the waxes to the coating surface.

Keyword : coating, permeability, postharvest handing, tangerines, waxing

INTRODUCTION

Fruit surface is covered with an epidermis protecting tissues inside from natural enemies such as pathogens and insects and also prevent water loss. The outer side of the epidermis is covered with cuticle layer consisting of wax and cutin. Cutin is thought to protect the fruit from microorganisms and insects. Wax, usually deposited on the outermost, is responsible for water loss prevention due to its hydrophobic nature (Cutter, 1978 and Esau, 1977). During harvesting and subsequent handling, wax may be loss due to rubbing among fruits or between fruit and other surfaces, and due to cleaning, sorting and sizing processes. Commercial wax is usually applied to the fruit surface to replace the missing natural wax. Waxed fruits respired at a reduced rate and lost less water and consequently had a longer shelf life than the normal fruit. They might also be polished and became shiny and attractive to the consumer. The attractiveness of waxed fruit was probably the main reason for coating fruits. In addition, fungicide or other chemical might be used together with wax to increase shelf life (Ben-yehoshua, 1987; Kaphan, 1986).

Coating materials are avaiable in the market in many forms and all are imported. They are usually mixture of different waxes. No scientific information about the properties of individual wax, in term of gas and vapor permeabilities, are available for farmer or packer to choose the suitable one for a specific commodity, except that reported by Hagenmaier and Shaw (1991 and 1992). However, they reported the permeablility of gases to different waxes, coated on plastic sheet instead of a fruit or vegetable. The present work was conducted in order to understand the gas and vapor permeability properties of shellac and carnauba wax, the two most basic componint of commercial fruit and vegetable coating, while coated on tangerines. Permeability of gases through both waxes coated on silk screen was also conducted.

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MATERIALS AND METHODS

The experiment was divided into 3 parts.

I. effect of carnauba and shellac coating on the gas and vapor exchange of tangerines.

Carnauba of highest commercial grade (melting point 82.5-83.5 C and shellac were used. The coating solutions were prepared by using morpholine oleic acid as the emulsifier and diluted with water to final concentrations between 0-20 % The coating were applied by hand on 10 tangerines per replication, 3 replications was used. All fruit were stored at 29+/-2 C and 73+/-4% relative humidity. On day 3,7 and 14 the fruit were evaluated for percent weight loss. Internal oxygen and corbon dioxide concentration was determined by drawing gas sample from the middle of tangerines with needle and syringe under water, and injected into a TCD gas chromatograph Shimadzu 14A. Molecular sieve 5A and Silica gel columns were used respectively. Internal alcohol content were detemined from the head space of 10 ml tangerine juice in 50 ml erlenmeyer flask using a FID gas chromatograph, with a Carbowax 20M column.

II. Effect of mixed wax on the gas and vapor exchange of tangerines.

Coating solutions were prepared from carnauba and shellac together at a total concentration of 12% and coated on tangerines. The evaluation for gas exchange property was done 9 days after storage at room temperature, as in section I.

III. Direct permeability of oxyen and carbon dioxide to carnauba and shellac coatings.

Coating solutions similar to that in the first secton were spreaded on silk screen. The screen was then passed through a pair of glass rods to spread out the wax evenly. The coated silk screen were left to dry and used for permeability tested by fitting into a permeability test chamber, which was consist of a pair of steel chambers screwed together and separated from each other only by the silk screen. On the lower chamber, oxygen free nitrogen was passed through, while on the upper chamber, 19.53% oxygen or 10.22% carbon dioxide balanced with nitrogen was passed through. The flow rate was constant and equal at 42 ml/min. on both side of the chamber. After 1 hour equilibration period,concentration of either oxygen or carbon dioxide on both side of the chamber was stabilized, gas sample was drawn from the lower chamber to determine for oxygen and carbon dioxide concentrations with a gas chromatograph in the similar manner to that in the first section. Permeation of gases to both coatings were calculated using formula P = Lc /Uc x 100, when P = percent of permeation, Lc = concentration in the lower chamber and Uc = concentration in the upper chamber.

RESULTS AND DISCUSSION

Uncoated tangerines lost 13% of their weight after 14 days (Figure 1). Coating with carnauba reduced weight loss to 5.0-7.6% with the highest concentration of carnauba gave highest weight loss reduction. Shellac coating gave poorer weight loss reduction than carnauba. All concentrations of shellac reduced weight loss similarly to about 9%. Internal oxygen concentration of uncoated fruit was about 16% after 14 days in storage (Figure 2A) carnauba coatings slightly reduced oxygen level to 13.0-14.8%. On the other hand, shellac coating dramatically reduced internal oxygen concentration to 5.3-9.0%. There was no different in oxygen level among fruit coated with different concentrations of carnauba. The same was true for shellac. Carbon dioxide concentration inside the control tangerines was 2.0% (Figure 2B), about the same as that inside tangerines coated with carnauba

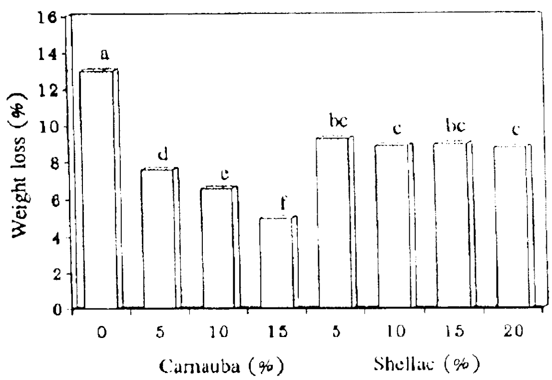

Figure 1 Weight loss of tangerines coated with various concentrations of carnauba and shellac, 14 days after storage at room timperature. Bars with the same letter was not significantly different by the Dancan New Multiple Range Test, at 95% level.

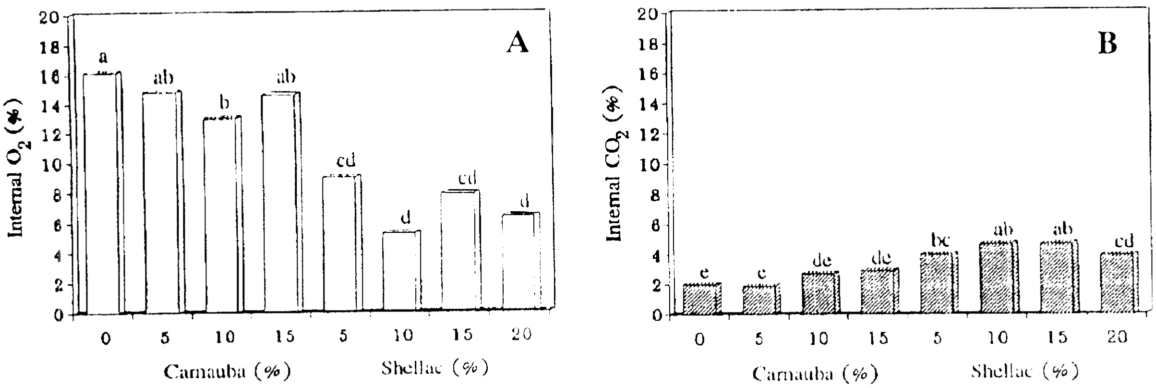

Figure 2 **Internal oxygen (A) and carbon dioxide (B) concentrations of tangerines coated with various concentrations of carnauba and shellac, 14 days after storage at room temperature. Bars with the same letter was not signigicantly different by the Dancan New Multiple Range Test, at 95% level.**

of all concentrations. On the other hand, carbon dioxide concentrations inside tangerines coated with shellac were between 3.9-4.7% not significantly different among different concentrations of shellac.

This result confirmed the finding by Hagenmaier and Shaw (1992) that: 1) Carnauba wax was good in preventing water loss, but was poor in limiting gas exchanges. These properties were opposite to that of shellac. The reason behind this differences might be due to chemical properties of the polymers. It was likely that water vapor molecules moved through polar material better than non-polar ones (Sha'afi, 1981). It was also shown that oxygen permeability to non-polar polymers was better than to the polar ones (Ashley,1985). Canauba composition consisted of alkyl ester of higher fatty acids, having 6% oxygen content, while shellac composition consisted of aliphatic and alicyclic hydroxy acids and their polyesters and has 20% oxygen content (Windholz *et al*, Hagenmaier and Shaw, 1992). 2)Carbon dioxide permeation through both coatings was better than oxygen, probably because carbon dioxide was more soluble in the polymers than oxygen (Pascat, 1986)

Ethanol concentration in the head space of tangerine juice extractd from uncoated tangerines and those coated with carmauba of all concentrations were not significantly different (Figure 3). Ethanol level were about 50-120 ppm. On the opposite, tangeines coated with shellac had significantly higher ethanol concentrations. At 15 and 20% shellac concentrations, ethanol content was as high as 650 ppm. The result agreed with the property of waxes in limiting gas exchange shown above. When oxygen was used for respiration and could not be replaced by oxygen from the external atmosphere, as in the case of shellac coating anaerobic respiration was induced and resulted in the accumulation of ethanol. It should be noted

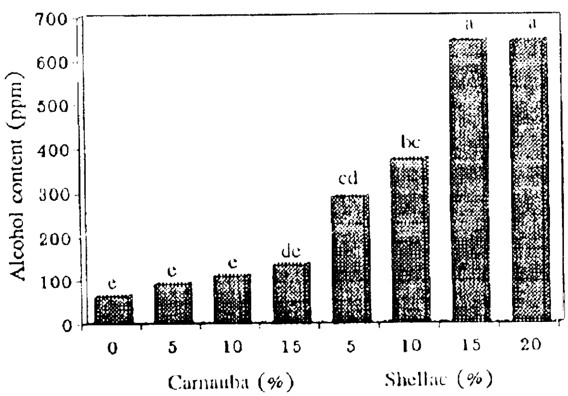

Figure 3 **Ethanol content in the head space of tangerine juice from tangerines coated with various concentrations of carnauba and shellac, 14 days after storage at room temperature. Bars with the same letter was not significantly different by the Dancan New Multiple Range Test, at 95% level.**

however that although oxygen and carbon dioxide levels in tangerines coated with various concentrations of shellac were not different, ethanol content inside the fruit increased with the concentraion of shellac. This discrepancy could be explained by the fact that oxygen and carbon dioxide concentrations were determined from the gas sample taken from the fruit cavity. It might not represent the real internal gas concentration, since the fruit cavity were connected directly with the stem end and the stylar end of the fruit, where gas exchange could occur easily. For the intercellular gas, however, the path for gas exchange might have to pass through the fruit surface, where waxes were applied. Barmore and Biggs (1972) reported that in oranges the exchange of carbon dioxide and ethylene through stem scar was twice that of the peel.

With the above finding, carnauba should be used on fruits that required good gas exchange such as citrus, which would develop off-flavor under low level of oxygen or high level of carbon dioxide conditions (Ben-yehoshua, 1987). Nevertheless carnauba was quite expensive, a substitute might be nesecessary to reduce the coating cost. Shellac is suitable for fruit which required less gas exchange, or reduced oxygen and elevated carbon dioxide conditions, such as most climacteric fruits. Low oxygen and high carbon dioxide condition inhibited respiration, ethylene producrtion and other ripening processes. However,shellac had a poor water barrier property so that the other mean to prevent water loss is necessary, such as the use of refrigeration or the use of a coating mixture.

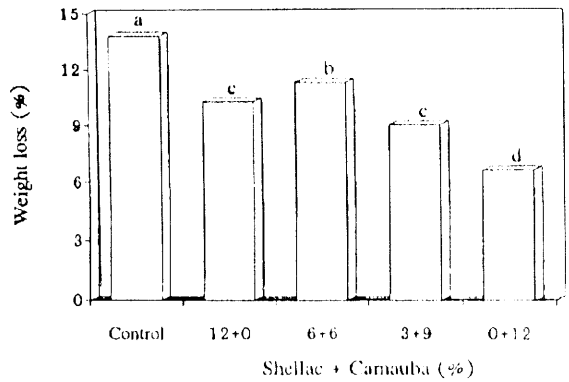

Figure 4 Weight loss of tangerines coated with mixtures of carnauba and shellac, 9 days after storage at room temperature. Bars with the same letter was not significantly different by the Dancan New Multiple Range Test at 95% level.

In the experiment testing properties of mixed coating between carnauba and shelalc, it was found that carnauba and shellac could not be mixed when shellac was 9% or higher, with a total concentration of 12%. The weight loss reduction property of mixed coatings fell in between the property of both waxes, but shellac seemed to have a stronger influence than the carnauba (Figure 4). At 6% shellac + 6% carnauba,

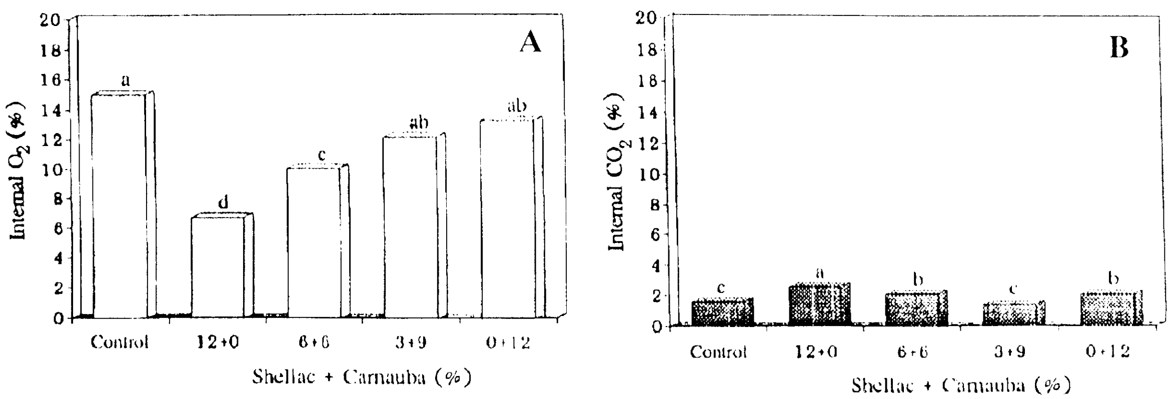

Figure 5 Internal oxygen (A) and carbon dioxide (B) concentration of tangerines coated with mixtures of carnauba coated with mixtures of carnauba and shellac, 9 days after storage at room temperature. Bars with the same letter was not signigicantly different by the Dancan New Multiple Range Test, at 95% level.

weight loss was 11.3% after 9 days of storage, which was close to the weight loss of control fruit and those coated with 12% shellac. Gas barrier property of mixed waxes also fell between the property of both waxes. Oxygen concentration inside tangerines coated with 6% shellac + 6% carnauba was 10%, about half way between the concentration of oxygen in tangerines coated with 12% carnauba or 12% shellac. Internal carbon dioxide concentrations were very close among coated or uncoated fruits. However, the concentration in 12% shellac coated was sinificantly higher than those coated with 12% carnauba. Similar finding was also found in the concentration of ethanol in the head space of tangerine juice. With 12% shellac coating ethanol concentration was very high (409 ppm). When carnauba was added, ethanol concentration lowered and was not statistically different from that in the control fruit. In addition, it was also found that all coating mixtures gave less shinning appearance tangerines than either carnauba or shellac alone. For fruits that needed a shinny appearance, a third component must be added to the mixture.

In the study on permeability of oxygen and carbon dioxide to carnauba and shellac coated on silk screen, it was found that at lower concentrations (10% and lower) of both coating, oxygen and carbon dioxide could move through the coating freely. This finding did not agree with the work done on tangerines in the first and second experiment. The reason was that at lower concentration both carnauba and shellac could not form a continueous film on the silk screen. The examination under microscope revealed that there are a number of tiny hole on the layer of wax coated on the silk screen. Gas could diffuse through these hales easily. The gas barrier property of both wax was found at 15% concentration and higher. Fifteen percent carnauba allowed oxygen and carbon dioxide to permeate by as much as 70%. For shellac at 15% concentration, oxygen permeation was reduced to only 12%, while it was only 3% for carbon dioxide. The result agreed with the first and second experiment that shellac was a better gas barrier than carnauba. It also supported the finding by Hagenmaier and Shaw (1991 and 1992). However, when compared between the permeability of oxygen and carbon dioxide, the result was opposite to the earlier findings which reported a better permeability of carbon dioxide than oxygen in all waxes tesed. In our experiment the thickness of the coating was as high as 80 μm much thicker than that usually found on coated fruits, which was about 1 μm (Ben-yeho shua *et al*, 1985). The technique using silk screen reported here might not be suitable of determining the permeability of the wax. However, the study did show that the property of coatings would depend also on the adhesion between the wax and the coating surface. This means that gas barrier of any wax coated on different fruit might not be the same. Hagenmaier and Shaw (1992) also reported that the permeability of gases depended on the other factors such as solvent and pH used in the preparation of the coating. The pH of the coating surface could also influence the permeability.

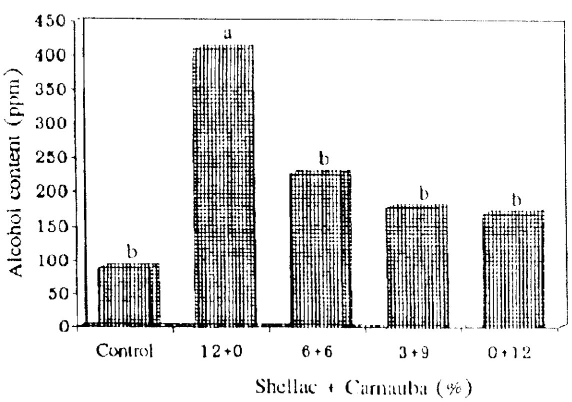

Figure 6 Ethanol content in the head space of tangerine juice from tangerines coated with mixtures of carnauba and shellac, 9 days after storage at room temperature. Bars with the same letter was not significantly different by the Dancan New Multiple Range Test, at 95% level.

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