CHAPTER 5
DISCUSSION

5.1 Effect of coating materials and storage temperatures on the physico-chemical and physiological characters of tangerine fruit

5.1.1 Weight loss

Effect of coating materials

Coating is a type of the modified atmosphere technology. The role of coating is to reduce water loss and increase the storage period of fruit. The weight loss of all commercially coated fruit was significantly less than that of the control fruit. The least weight loss was exhibited by the Fomesa coating followed by Citrashine, Supershine-C, Zivdar, Citrosol AK, and Perfect Shine. Weight loss is mainly caused by fruit transpiration in which water moves out of the fruit by vapor phase diffusion driven by a gradient of water vapor pressure between inside and outside of the fruit.

Transpiration is a physical process that can be controlled by various postharvest treatments which are applied to the commodity (surface coatings and other moisture barriers) or which involve manipulation of the environment such as maintenance of high relative humidity (Kader, 2006). Water loss through transpiration not only results in direct quantitative losses (loss of saleable weight), but also causes losses in appearance (wilting, shriveling), textural quality (softening, flaccidity, limpness, loss of crispness and juiciness), and nutritional quality.

Some surface coatings are like the waxy natural fruit surface in that they are good barriers to water vapor. The reason for the reduction in weight loss may be due to the blockage of lenticels and/or stomates as evidenced by the reduction in respiration and gas exchange (Hagenmaier and Baker, 1993c).

The commercial microemulsion coatings containing oxidized polyethylene wax and oleic acid were relatively successful in controlling water loss (Hagenmaier and Baker, 1997). Hagenmaier (2000) mentioned that the weight loss was markedly lower for the ‘Valencia’ oranges coated with polyethylene-candelilla wax coating than the HIGLOSS coating (shellac and wood rosin). Mean rates of weight loss at 21-25°C were about 0.25%/day for the HIGLOSS coating. The washed-unwaxed ‘Valencia’ orange and polysaccharide-coated fruit exhibited a weight loss of 7.7±0.8 to 8.9±0.3%, whereas shellac-coated fruit lost only 5.5±0.2% of their total weight after 2 months of storage at 20°C (Baldwin *et al*., 1995a, b).

The rate of water loss can be reduced by 30% to 50% with the use of some waxes (Wills *et al*., 1998). Carnauba wax and shellac are good barriers of moisture loss, whereas polyethylene has higher permeability of water vapor (Hagenmaier and Baker, 1993a; Hagenmaier and Shaw, 1992). ‘Sazuma’ mandarin coated with Britex 505, PacRite-StorRite 101 (contained polyethylene and shellac), Primafresh 30 (contained carnauba wax and shellac), Decco Lustr 202 (contained natural and synthetic waxes and fatty acids), and Natural Zivdar (contained a carnauba wax emulsion) had lower weight loss than non-coated fruit during storage at 15°C for 28 days (Mannheim and Soffer, 1996). Two types of pummelo (‘Kao Phuang’ and ‘Siamese’) coated with ammonia-based candelilla, shellac and carnauba wax formulations were used at two different concentrations (20% and 10% total solids) had lower weight loss than non-coated control (Hagenmaier, 2004). Mandarins cv. ‘Clemenules’ coated with coatings consisted on polysaccharide and shellac-beeswax at the following concentrations and ratios: (1) 78% shellac : beeswax (14:1); (2) 73% shellac : beeswax (4.6:1); (3) 50% shellac : beeswax (1:1), all coated fruit delayed dehydration during storage for 4 weeks at 4ºC plus 1 week at 20ºC (Pérez-Gago *et al*., 2003a). Coated ‘Fortune’ mandarins with 18.7% hydroxypropyl methylcellulose + 60% beeswax + 12.0% stearic acid + 9.3% glycerol + 1% NH_3, 18.7% hydroxypropyl methylcellulose + 60% carnauba wax + 12.0% stearic acid + 9.3% glycerol + 1% NH_3 and 18.7% hydroxypropyl methylcellulose + 60% shellac + 12.0% stearic acid + 9.3% glycerol + 1% NH_3 had lower weight loss than uncoated mandarins under 4 weeks at 9°C followed by 1 week at 20°C (Pérez-Gago *et al*., 2002).

Mandarin fruit cv. ‘Nova’ and ‘Michal’ coated with 82.9% water + 0.5% xanthan gum + 10% carnauba wax + 2% shellac + 1.8% oleic acid + 2.4% morpholine, 82.9% water + 0.5% guar gum + 10% carnauba wax + 2% shellac + 1.8% oleic acid + 2.4% morpholine, 82.9% water + 0.5% locust bean gum + 10% carnauba wax + 2% shellac + 1.8% oleic acid + 2.4% morpholine and 83.4% water + 10%

carnauba wax + 2% shellac + 1.8% oleic acid + 2.4% morpholine and commercial coating were much better controlling weight loss than control fruit after storage for 1 month at 5°C and 73% relative humidity (Chen and Nussinovitch, 2000a). Coated 'Ortanique' mandarin fruit with 26.7% hydroxypropyl methylcellulose + 40% beeswax + 13.3% glycerol + 20.0% stearic acid, 26.7% hydroxypropyl methylcellulose + 40% beeswax + 13.3% glycerol + 20.0% palmitic acid and 26.7% hydroxylpropyl methylcellulose + 40% beeswax + 13.3% glycerol + 20.0% oleic acid, compared to the control reduced weight loss during storage at 5°C for 7 weeks up to 30% (Navarro-Tarazaga *et al*., 2008).

Effect of temperatures

Temperature and humidity are critical in minimizing the difference in water vapor pressure between product and environment (Kays and Paull, 2004). Low temperature and high relative humidity storage can slow down and reduce water loss of the fruit.

Coated tangerine fruit stored at 5 and 10°C can reduce weight loss better than fruit stored at room temperature. Increasing the product temperature increases the free energy of the water molecules, which increases their movement and potential for exchange. From the heat given off during respiration, stored products normally have a slightly higher temperature than the surrounding atmosphere, which enhances water loss (Kays and Paull, 2004). Temperature also affects the amount of moisture that can be held in the air surrounding the product. As the temperature decreases, the maximum amount of moisture that can be held by the air also decreases. Fluctuations in temperature can result in a much more rapid water loss from stored products than a constant temperature (Kays and Paull, 2004).

The relationship between humidity and water exchange is relatively straightforward, temperature effects are more complex. Three thermal parameters have a pronounced effect on moisture exchange in storage: the actual temperature, the differential in temperature between product and environment and fluctuations in storage temperature. Lowering the temperature decreases the maximum amount of water the air will hold; if the weight of water vapor in the air is held constant, the relative humidity will increase. The water vapor pressure deficit between a product and its environment will also decrease at a given relative humidity with decreasing temperature. Therefore, low temperature decreases the rate of water loss. Waxes, along with high humidity and refrigeration, have traditionally been used to reduce moisture loss from fresh citrus fruit during transit and storage (Kays and Paull, 2004).

Porat *et al.* (2005) who observed that 'Mor' mandarins coated with Tag with 5% polyethylene solids, Tag with 9% polyethylene solids, Tag with 13% polyethylene solids, Commercial Tag (18% polyethylene solids), Tag with half shellac and Tag without shellac had lower weight loss than control fruit after 4 weeks of storage at 5°C and 5 more days under shelf life conditions at 20°C. Purvis (1983) mentioned that waxed and seal-packaged 'Hamlin' oranges and 'Marsh' grapefruit lost moisture lower than control fruit during storage at 5°C. Several commercial microemulsion coatings containing oxidized polyethylene wax and oleic acid were relatively successful in controlling fluid loss of 'Ruby Red' grapefruit during storage at 2°C for 4 weeks (Hagenmaier and Baker, 1997).

5.1.2 Gloss

The results showed that tangerine fruit coated with commercial coatings had higher gloss unit than those coated with chitosan solutions and non-coated fruit. By observation with the naked eye, the gloss of all coatings decreased during storage but remained higher than the uncoated fruit.

Appearance is the most important quality attribute of fresh produce, with primary concern for size and color uniformity, glossiness, and absence of defects in shape or skin finish (Aked, 2000). Commercial applications of wax coatings is rather extensive on citrus, apples, mature green tomatoes, rutabagas, cucumbers, and other vegetables such as asparagus, beans, beets, carrots, celery, eggplant, kohlrabi, okra, parsnips, peppers, potatoes, radishes, squash, sweet potatoes, and turnips (Hardenburg, 1967), where high glossing and shine surface are desired. Waxes-based coatings are continuously evaluated for their applications in citrus fruit, melons, and some tree fruit such as apples and pears (Hagenmaier and Baker, 1997; Alleyne and Hagenmaier, 2000; Hagenmaier, 2000; Bai *et al.*, 2003a, b; Fallik *et al.*, 2005; Porat *et al.*, 2005).

Dou *et al.* (1999) reported that the shine of 'Marsh' grapefruit coated with shellac/resin solutions or carnauba waxes were similar in all treatments and higher than non-coated fruit. Shellac significantly increased 'Valencia' orange fruit shine in comparison to either non-coated fruit or fruit coated with polyethylene or carnauba, carnauba and polyethylene coatings increased fruit shine compared to non-coated fruit (Dou *et al.*, 2001). Coated 'Fortune' mandarin fruit with 20% beeswax, 20% carnauba wax, 20% shellac, 60% beeswax, 60% carnauba wax and 60% shellac had a nice shine and gloss than non-coated fruit under commercial storage conditions at 20°C (Pérez-Gago *et al.*, 2002). Chen and Nussinovitch (2000b) reported that the best gloss of coated citrus fruit cv. 'Nova' and 'Michal' with commercial coating, but no significant differences between fruit coated with locust bean gum, xanthan gum, guar gum and carnauba-shellac wax. Hagenmaier and Baker (1994a) and Hagenmaier (2000) also observed a decrease in gloss with storage time in 'Valencia' oranges coated with wax microemulsions as being more important in shellac-based than wax-based coatings. 'Clementine' mandarin coated with commercial wax A (100 g/kg total solids of polyethylene wax and shellac), diluted commercial wax A with 70 g/kg total solids, commercial wax B (100 g/kg total solids of polyethylene wax and shellac) and diluted commercial wax B with 70 g/kg total solids had higher peel gloss than non-coated fruit. Peel gloss of mandarin fruit decreased with longer storage period at 5°C and 90% relative humidity (Marcilla *et al.*, 2009). Valencia-Chamorro *et al.* (2009) mentioned that hydroxypropyl methylcellulose (HPMC)-lipid edible composite coatings provided higher gloss of 'Valencia' oranges than the uncoated control during storage for 60 days at 5°C plus 7 days at 20°C.

5.1.3 Internal gases

Effect of coating materials

Fruit coated with different commercial coatings, polyethylene microemulsion and chitosan solutions had lower internal O_2 and higher internal CO_2 concentrations than non-coated fruit. The results also showed that non-coated tangerine fruit had the highest internal O_2 concentration, which significant different from fruit coated with Zivdar, Citrashine and Fomesa by commercial method. Fruit coated with Zivdar had higher internal O_2 concentration than those coated with Fomesa and Citrashine. Fruit coated with Citrashine and Fomesa had the highest internal CO_2, followed by fruit coated with Zivdar. While, non-coated fruit had the lowest internal CO_2

concentration during storage. The results also indicated that there was a correlation between low concentrations of O_2 and high CO_2 concentrations of tangerine fruit.

The internal O_2 concentration of tangerine fruit coated with formulation A, B, C, D and Zivdar were not significant different. There was a similar trend in the reduction of internal O_2 concentration in all coated treatments. The control treatment was found to be significantly higher O_2 concentration throughout the observation period. There were no significant differences among internal CO_2 concentration of tangerine fruit coated with coating formulation A, B, C, D and Zivdar and non-coated fruit had the lowest internal CO_2 concentration.

When coatings are applied to fruit, they form an additional barrier through which gases must pass. Because coatings differ in gas permeance and ability to block openings in the peel, coatings resulted in reducing gas exchange between the atmosphere and internal tangerine fruit (Hagenmaier and Baker, 1993a). Therefore, the amount of internal O_2 reduced, while the amount of internal CO_2 increased (Hagenmaier and Baker, 1994b; Petracek *et al.*, 1998). Furthermore, internal gas composition was highly dependent on coating type and thickness. However, it is still not clear how these factors interact in relation to the internal modified atmospheres of coated produce (Cisneros-Zevallos and Krochta, 2003).

Coatings with low permeability offer more of a barrier to gas exchange between the fruit and external atmosphere, resulting in a modified internal fruit atmosphere of relatively high CO_2 and low O_2, whereas excessive modification can cause anaerobic metabolism (Hagenmaier, 2002). In previous works, the effects of different types of wax on gas permeability and anaerobic conditions were studied in various orange and mandarin varieties. It was concluded that wax-based coatings, especially for polyethylene-based, are much more permeable than carnauba-, shellac-, and wood rosin-based coatings and are more suitable for coating mandarins (Hagenmaier, 2000; Hagenmaier and Baker, 1993a, b, 1995; Hagenmaier and Shaw, 1992; Mannheim and Soffer, 1996).

Shellac and wood rosin content are common used as the coating ingredient, which most affected internal quality of the tangerine fruit. Citrashine (shellac-based wax) and Fomesa (10% oxidized polyethylene wax + 8% glycerol ester of wood rosin + 2% ammonium hydroxide), contain high concentration of shellac and wood rosin.

The shellac evidently restricted the exchange of O_2 and CO_2 between the atmosphere and tangerine to such an extent that internal O_2 concentration became too low and resulting in high levels of internal CO_2 (Cohen *et al*., 1990b; Baldwin *et al*., 1995a,b).

Coatings with shellac and rosin generally have lower permeability to CO_2, O_2 and ethylene gases while coatings made with polyethylene wax have high permeability to such gases compared to those made with carnauba and other waxes. Permeability to O_2 is also affected by percentage of relative humidity and polar components used to raise pH and solubilize a polymer such as shellac (Hagenmaier and Shaw, 1992). Hagenmaier and Baker (1995) reported that values of internal CO_2 and O_2 were most like uncoated control for 'Marsh' grapefruit and 'Valencia' orange with wax coatings (polyethylene-based coatings) (Hagenmaier and Shaw, 1992).

Hagenmaier (2005) mentioned that 'Valencia' orange coated with 590HS, candelilla, Brilliance and polyethylene and stored at 20°C had lower internal O_2 and higher internal CO_2 than non-coated fruit. Moreover, it was found that 2-fold differences internal CO_2 and several fold differences in internal O_2 between shellac- and wax-coated citrus fruit (Hagenmaier and Baker, 1994b). Mannheim and Soffer (1996) used Natural Zivdar (contained a carnauba wax emulsion), Primafresh 30 (contained carnauba wax and shellac) and PacRite-Sun-Shine (contained shellac) to coat 'Valencia' oranges and reported that treated oranges had lower O_2 and higher CO_2 concentrations than the control fruit. Petracek *et al*. (1998) reported that grapefruit coated with carnauba, polyethylene, shellac 1, shellac 2 and shellac 3 had lower internal O_2 and higher CO_2 than non-coated grapefruit. Hagenmaier and Grohmann (1999) showed that fruit coated with commercial coating, shellac-based coatings, those with food-grade polyvinyl acetate (PVA) coatings had relative higher internal O_2 and lower internal CO_2 concentrations.

Pérez-Gago *et al*. (2002) reported that coating application to 'Fortune' mandarins increased internal CO_2 and decreased O_2, which indicates the creation of an internal atmosphere when compared to uncoated mandarins. Shellac-based coatings induced the higher CO_2 accumulation in fruit stored at 20°C. This is consistent with the high gas barrier that shellac provides, as compared to waxes such as beeswax and carnauba wax (Hagenmaier and Baker, 1994b). Internal O_2 concentration was lower in white 'Marsh' grapefruit coated with shellac waxes compared to resin solution coated fruit after 10 days of storage at 21°C and 93% relative humidity (Dou *et al*., 1999). Three coatings groups (carnauba, polyethylene and shellac) application tended to reduce internal O_2 and increased internal CO_2 concentrations in ‘Valencia’ orange fruit after 5 months storage at ~4°C (38°F) (Dou *et al*., 2001). Coatings application to ‘Ortanique’ mandarins increased internal CO_2 and decreased O_2 contents compared to uncoated fruit, which indicates the creation of an internal modified atmosphere after 6 weeks storage at 5°C followed by 1 week at 20°C (Navarro-Tarazaga *et al*., 2008). Internal O_2 levels were low for grapefruit coated with shellac-based waxes (1.8-3.5%), higher for polyethylene- and carnauba-based waxes (9.5 and 10%, respectively) and the highest for non-waxed fruit (19.0%). Conversely, internal CO_2 levels were high for grapefruit coated with shellac-based waxes (7.8-8.3%), lower for fruit coated with polyethylene and carnauba-based waxes (5.8 and 4.9%, respectively), and the lowest for non-waxed fruit (1.5%) after storage for 28 days at 21°C and 93% relative humidity (Petracek *et al*., 1998).

Coated ‘Valencia’ oranges had lower internal O_2 and higher CO_2 than uncoated fruit, commercial shellac-based coated fruit having the lower O_2 and higher and CO_2 than commercial polysaccharide-based coated fruit during storage at 21°C (Baldwin *et al*., 1995c). Coating treatments (Coseal wax, beeswax A, beeswax B and 1.5% chitosan) resulted in higher internal CO_2 levels and lower internal O_2 levels of ‘Satsuma’ mandarin compared to uncoated fruit after storage at 5°C for 24 hours (Ko *et al*., 2008). The CO_2 for resin and shellac coatings becomes markedly higher, whereas CO_2 is little affected by thickness of waxed-based coatings. Internal gas concentrations of ‘Valencia’ oranges were markedly different for polyethylene-candelilla-wax coating formulation and a HIGLOSS (shellac and wood rosin) coating. Oranges coated with HIGLOSS and stored 9-16 days at 21-25°C had internal O_2 values of 0.7-0.9% and internal CO_2 of 17-22%. Oranges with the wax coating had internal O_2 of 8-11% and internal CO_2 of 5-7% (Hagenmaier, 2000). Valencia’ orange and ‘Marsh’ grapefruit coated with Brogdex 555 coating (high-gloss shellac) had lower internal O_2 and higher CO_2 than fruit with the wax coating (consisting of 12.0% polyethylene, 4.0% candelilla wax, 3.2% oleic acid, 0.8% myristic acid, and 0.9% NH_3, with 500 mg/kg thiabendazole) after kept in cold storage for 1-5 months, oranges at 1°C with 97% relative humidity and the grapefruit at 3°C with 70% relative humidity or 7°C with 75% relative humidity (Hagenmaier *et al*., 2002).

Effect of storage temperatures

The results demonstrated that tangerine fruit stored at 5 and 10°C had higher internal O_2 and lower internal CO_2 than fruit stored at room temperature. The exchange of gases between atmosphere and internal fruit depends on the storage environments such as temperature and humidity (Baldwin *et al*., 1995a, b). Different storage temperatures seem to affect coating performance in terms of increasing internal CO_2 and especially decreasing internal O_2 concentrations. The lower storage temperature (3-10°C) resulted in minor increases in internal CO_2 and negligible decreases in internal O_2 concentrations whereas at the higher storage temperature, increases in internal CO_2 were greater while internal O_2 levels were drastically reduced (Banks, 1985). These differences in internal gas changes due to storage temperature are probably related to the effect of temperature on fruit respiration (Krochta *et al*., 1994).

5.1.4 Respiration rate

Statistical analysis showed a significant difference between control and coated samples for respiration rates. The control fruit had a higher respiration rate than coated tangerine fruit. Supershine-C coating provided the lowest respiration rate compared with others. The production of CO_2 for the coated fruit was lower than in the control. The suppression of respiration was likely the result of the modification of the internal atmosphere of the fruit (decreasing O_2 and increasing CO_2) caused by the semipermeable characteristics of the coatings to these gases (Banks, 1984a, b). Reduction of the respiration rate as a result of coatings has also been reported for cherries (Martinez-Romero *et al*., 2006) and strawberry (El-Ghaouth *et al*., 1991a, b).

The fruit coated with 9 commercial coatings, PE microemulsion and 2.0% chitosan did not show any significant difference in the respiration rate, but lower than fruit coated with 1.5% chitosan and non-coated control fruit. In addition, the results indicated that non-coated fruit had the highest respiration rate throughout the storage period.

Respiration can be described as the oxidative breakdown of the more complex materials normally present in cells, such as starch, sugars and organic acids, into simpler molecules, such as CO_2 and water, with the concurrent production of energy and other molecules that can be used by the cell for synthetic reactions. Respiration can occur in the present of O_2 (aerobic respiration) or in the absence of O_2 (anaerobic respiration or fermentation) (Wills *et al*., 2007).

The organic substrates broken down in aerobic respiration may include carbohydrates, lipids, and organic acids. Increases in CO_2 and decreases in O_2 concentrations exert largely independent effects on respiration and other metabolic reactions. Generally, the O_2 concentration must be reduced to less than 10% (by volume) before any retardation of respiration is achieved (Wills *et al*., 2007).

Respiration is widely assumed to be slowed down by decreasing available O_2 as a consequence of reduction of overall metabolic activity (Kader, 1987; Solomos and Kanellis, 1989). The reduction in O_2 concentration that is necessary to retard respiration depends on the storage temperature. As the temperature is lowered the required concentration of O_2 is also reduced. The critical O_2 level beyond which anaerobic respiration occurs is determined mainly by the rate of respiration; therefore it is greater at higher temperatures (Wills *et al*., 2007).

The idea of respiratory inhibition by CO_2 was first supported by simple explanations, i.e., that CO_2 was a product of the respiration process and, caused simple feedback inhibition (Herner, 1987). Another hypothesis considered that CO_2 had a strong controlling effect on mitochondrial activity, including citrate and succinate oxidation. The elevated CO_2 might affect the Krebs cycle intermediates and enzymes (Kader, 1989). High CO_2 might inhibit C_2H_4 production rather than having a direct effect on the respiration process (Kubo *et al*., 1989). Waxing generally reduces the respiration and transpiration rates (Verma and Joshi, 2000).

The results of coated tangerine fruit in this experiment indicated that all coatings reduced steady-state of respiration rate in tangerine fruit. The trend towards higher CO_2 and lower O_2 that characteristics coated fruit correlates with observed lower respiration rates, and emphasizes the influence of the coating-mediated modified internal atmosphere on fruit respiration rate (Alleyne and Hagenmaier, 2000). Chun *et al.* (1998) reported that Satsuma mandarin cvs. ‘Miyakawa’ and

'Hayashi' were divided into four groups: control, seal in polyvinyl chloride (PVC) wrap, coated with carnauba wax and coated with polyester of fatty acids kept at 4, 10 and 20°C. Sealing or coating treatments maintained an internal atmosphere of lower O_2 and higher CO_2 and reduced apparent respiration rate compared with the unsealed and uncoated control fruit. 'Valencia' orange fruit waxed with 25% *trans* jojoba oil showed equal respiration rate with export wax treatment during storage at 5°C for 60 days, while control fruit had the highest respiration rate compared to the initial value at harvest (Ahmed *et al*., 2007). The respiration rate of uncoated 'Satsuma' mandarin was higher than those coated with beeswax-A, beeswax-B and 1.5% chitosan during storage at 5 and 20°C (Ko *et al*., 2008).

5.1.5 Fermentative products

Lowering the O_2 level around fresh fruit and vegetables reduce their respiration rate in proportion to the O_2 concentration. However, minimum of about 1-3% O_2, depending on the commodity, is required to avoid a shift from aerobic to anaerobic respiration. Under such conditions, the glycolytic pathway replaces the Krebs cycle as the main source of the energy needed by the plant tissues. Pyruvic acid is no longer oxidized but is decarboxylated to form acetaldehyde, CO_2, and ethanol; this results in developing of off-flavors and tissue breakdown (Kader, 1986).

Elevated CO_2 concentrations also reduce that respiration rate of fresh fruit and vegetables, depending on the commodity and the O_2 concentration. High CO_2 can result in accumulation of acetaldehyde and ethanol within the tissues (Kader, 1986). CO_2 concentrations of about 10% resulted in formation of aldehyde and ethanol in black currants (Smith, 1957), mango fruit (Lakshminarayana and Subramanyam, 1970) and citrus fruit (Davis *et al*., 1973).

The flavor of tangerine and related citrus fruit is generally more sensitive to storage than other citrus varieties, possibly because of their relatively short maturation period (Davis, 1970; Grierson and Ben-Yehoshua, 1986; Cohen *et al*., 1991). Different researchers report that waxing and stored at high temperatures increase juice ethanol and CO_2 level and internal O_2 depletion (Davis and Hofmann, 1973; Hagenmaier and Baker, 1994b; Hagenmaier, 2002). The application of wax blocks enough gas exchange to decrease the concentration oxygen to the point where aerobic respiration is at least partially replaced by anaerobic fermentation (Kays, 1991).

5.1.5.1 Acetaldehyde content in juice

Flavors and aromas play an important role in evaluating their quality. Fruit flavor and aroma influence postharvest life as well. Flavor changes in plant material are the results of change in their biosynthetic pathways, regulatory mechanisms and volatile components which are involved in fruit flavor and aroma changes. These changes influence the postharvest acceptability and shelf life in sensory perspective (Galili *et al*., 2002).

Postharvest storage of oranges and mandarins exhibit rapid changes in internal volatiles including, ethanol, methanol, acetaldehyde, ethylacetate, 2-butanone, methylbutyrate, hexanal, 1-haxanol, alpha- and beta-pinene, limonene, octanal, nonalol, ethyloctanoate and valencene, especially, when they are coated with wax emulsions (Hagenmaier and Baker, 1994b). Magnitude of internal volatiles are correlated with postharvest wax application, a standard practice for reducing weight loss and imparting gloss to the citrus fruits. Complex natures of wax microemulsions used in different fruit coatings are responsible for build up of internal volatiles in different citrus cultivars (Hagenmaier, 1998a).

Postharvest wax application results in modified fruit respiration which alters the normal glycolysis pathway (aerobic to anaerobic). Anaerobic fermentation takes place in the uncoated fruit as well but rate of off-flavor development is much faster in coated fruit. In anaerobic respiration, fermentation results in the formation of series of metabolites but two early metabolites i.e., acetaldehyde and ethanol are reported in larger quantities (Petracek *et al*., 1997). Ethanol produced in citrus fruits is reduced product of acetaldehyde which results in change of aroma, i.e., from pleasant to unpleasant (Pérez-Gago *et al*., 2003a, b).

The results indicated that the amount of acetaldehyde of tangerine fruit coated with 4 development coatings (formulation A, B, C and D), Zivdar and non-coated fruit were not detected after storage for 10 days at room temperature.

Acetaldehyde, the precursor of ethanol, accumulates in almost every type of fruit during ripening (Fidler, 1968) and is one of the natural aroma compounds.

However, the potentia1 toxicity of the accumulated ethanol and acetaldehyde must be considered (Jackson *et al*., 1982; Perata and Alpi, 1991) and of active oxygen species formed upon re-exposure of the tissue to oxygen.

Among citrus varieties, mandarins are the most perishable and have a shorter potential storage life than oranges, grapefruit and lemons (Kader, 2002). Furthermore, mandarins are also much more likely to develop off-flavors after harvest; for example, after being coated with various waxes they produce more ethanol and acetaldehyde than other varieties (Cohen, 1999; Hagenmaier, 2002; Hagenmaier and Shaw, 2002).

Ethanol fermentation is a two-step process in which pyruvate is first decarboxylated to acetaldehyde by pyruvate decarboxylase and acetaldehyde is subsequently converted to ethanol by alcohol dehydrogenase. The off-flavor volatiles acetaldehyde and ethanol normally accumulate at low levels during fruit maturation and ripening, and thereby play an important role in the biosynthesis of fruit aroma volatiles (Shi *et al*., 2007). Unfortunately, such conditions may occur following application of wax coatings that restrict gas exchange through the peel layer (Hagenmaier, 2002); during storage under controlled or modified atmospheres containing low O_2 or high CO_2 levels (Ke and Kader, 1990); following implementation of quarantine treatments involving exposure to anaerobic atmospheres (Shellie *et al*., 1997); under inappropriate storage conditions, such as high temperatures and inadequate ventilation, that cause a reduction in O_2 levels (Waks *et al*., 1985); and after exposure to ethylene and stresses (Kimmerer and Kozlowski, 1982).

Chen and Nussinovitch (2000a) explained that after 30 days of storage at 5°C and 73% relative humidity plus one week at 19°C and 44% relative humidity, 6.8-31.8 mg/l acetaldehyde were detected in the juice of 'Nova' mandarin fruit coated with 10% carnauba wax + 2% shellac + 0.5% xanthan gum, 10% carnauba wax + 2% shellac + 0.5% guar gum, 10% carnauba wax + 2% shellac + 0.5% locust bean gum, 10% carnauba wax + 2% shellac, commercial coating (~18% dry matter of polyethylene and shellac) and non-coated control, and no significant among treatments were observed.

Acetaldehyde buildup in coated and non-coated mandarin fruit cv. 'Nova' is reported by Chen and Nussinovitch (2000a). After 30 days of storage at 4°C and 68%

relative humidity, 2.2-4.4 mg/l acetaldehyde were detected in the fruit juice. No significant differences were observed among the fruit coated with 6% carnauba + 0.5% xanthan gum, 5% carnauba + 0.5% xanthan gum, 5% carnauba + 1.0% xanthan gum, 4% carnauba + 1.5% xanthan gum, commercial coating (~18% dry matter of polyethylene and shellac) and control fruit. After the additional 7 days at room temperature (17°C and 71% relative humidity), the fruit coated with commercial formulation contained the highest concentration of acetaldehyde (21.9 mg/l), while the treatments made up of 4% carnauba + 1.5% xanthan gum and the control were found to contain the least acetaldehyde.

Valencia-Chamorro *et al*. (2009) reported that there was no significant differences in acetaldehyde contents of 'Valencia' oranges among hydroxypropyl methylcellulose + potassium sorbate, hydroxypropyl methylcellulose + sodium benzoate, hydroxypropyl methylcellulose + sodium propionate, hydroxypropyl methylcellulose + potassium sorbate + sodium propionate, hydroxypropyl methylcellulose + sodium benzoate + potassium sorbate, hydroxypropyl methylcellulose + sodium benzoate sodium propionate + and control fruit. The amounts of acetaldehyde lower than 6 mg/l were found on both coated and uncoated fruit after 60 days of storage at 5°C plus 7 days at 20°C.

5.1.5.2 Ethanol content in juice

Effect of coating materials

Ethanol content of the juice from coated fruit varied considerably for each coating treatment and increased during storage. Non-coated fruit showed the lowest ethanol content.

For developed coatings, ethanol content was significantly lower in juice from fruit coated with formulation D than fruit coated with formulation A and B. Non-coated control had the lowest ethanol content in juice. There were no significant differences of coated fruit among formulation D, formulation C and Zivdar. The results indicated that ethanol concentration differed greatly in coated treatments throughout the whole storage period with respect to the non-coated one. Ethanol levels in juice for coated and uncoated tangerines are significantly different due to creation of a modified atmosphere, as can be seen by the lower ethanol accumulation during storage in uncoated fruit than in coated fruit.

The coatings that are applied to fruit form barriers to the passage of O_2 and CO_2 through the fruit peel (Hagenmaier, 2005). Ethanol content in the coating application was notably higher as a result of the amount of rosin (shellac or wood rosin) formulations than that of wax (polyethylene- or carnauba-based) coatings and control fruit. With a lower permeability to gases, shellac and wood resin coatings result in lower internal O_2, higher internal CO_2, and a subsequent build-up of acetaldehyde and ethanol under anaerobic conditions, which leads to off-flavor in citrus fruit (Baldwin *et al.*, 1995c; Cohen *et al.*, 1990b; Hagenmaier, 2000, 2002). Ahmad and Khan (1987) found significant amounts of ethanol in waxed mandarins accompanied with a change in flavor. These researchers attributed the off-flavor to an insufficient supply of O_2 through the wax coating, which caused partial anaerobic respiration.

Citrus fruit with shellac-based coatings generally have been reported as having higher ethanol content than fruit with polyethylene and carnauba wax coatings (Hagenmaier and Baker 1994a; Hagenmaier, 2000). Glossy fruit coatings play an important role in development of off-flavor compounds as compared to less shine producing fruit coatings. The ethanol contents in 'Valencia' oranges with high-gloss shellac coating increase markedly during storage (Cohen *et al.*, 1990b). Uncoated fruit produce less ethanol (7.0 mg/kg/week) where as rate of ethanol production increase in high-gloss coated fruit (48 mg/kg/ week). In grapefruit and oranges coated with high gloss coating, the results indicated that half of the samples contain ethanol >1,000 mg/kg and 14% of the grapefruit and 45% of the orange samples having >2,000 mg/kg ethanol (Ahmad and Khan, 1987; Hagenmaier, 2002).

Ethanol concentration of tangerine juice extracted from uncoated and those coated with 0, 5, 10 and 15% carnauba concentrations were not significantly different after storage for 14 days at room temperature (ethanol content were about 50-120 mg/l). On the opposite, tangerines coated with shellac had significantly higher ethanol concentrations. At 15 and 20% shellac concentrations, ethanol content was as high as 650 mg/l (Chittarom and Siriphanich, 1993). In addition, grapefruit coated with shellac 1, shellac 2 and shellac 3 stored at 21°C for 14 days, the amount of ethanol was higher than non-coated grapefruit (Petracek *et al*., 1998). ‘Mor’ mandarin were coated with Commercial Tag and Modified Tag coatings and kept at 5°C for 5 weeks followed by holding at 20°C for 5 days, had higher ethanol content in juice than non-coated fruit (Porat *et al*., 2005). Ethanol, methanol and linalool increased roughly 2-fold at both 16 and 21°C in shellac-coated ‘Valencia’ orange fruit compared to uncoated control by the end of the storage period (Baldwin *et al*., 1995c).

The HIGLOSS (shellac and wood rosin) coated orange fruit cv. ‘Valencia’ stored at 21-25°C had higher ethanol content. The rate of increasing of ethanol for these treatments was 420±56 and 300±45 mg/l/day, respectively. By comparison, the ethanol content of the oranges coated with wax coatings (polyethylene-candelilla) increased by only about 70±21 and 60±12 mg/l/day, at storage temperature of 25 and 21°C, respectively (Hagenmaier, 2000). Minimal changes were observed with unwaxed fruit (Baldwin *et al*., 1995c).

‘Clemenules’ mandarins coated with commercial water wax A (100 g/kg total solids of polyethylene wax and shellac), diluted commercial water wax A with 70 g/kg total solids, commercial water wax B (100 g/kg total solids of polyethylene wax and shellac), diluted commercial water wax B with 70 g/kg total solids and non-coated fruit after 62 days of 5°C storage. Ethanol content of averaged was around 2,200 mg/l, while mean for each treatment was not higher than 1,700 mg/l (Marcilla *et al*., 2009). The concentration of ethanol in the juice of coated ‘Valencia’ oranges after both storage for 30 days at 5°C followed by 7 days at 20°C or 60 days at 5°C followed by 7 days at 20°C was in the range of 1,040-1,240 mg/l, while it was in the range of 770-866 mg/l in uncoated samples (Valencia-Chamorro *et al*., 2009).

Effect of storage temperatures

Storage of tangerine fruit at room temperature resulted in the higher amount of ethanol content in juice than the fruit stored at 10 and 5°C for about 2-3 times, respectively. The storage period for 10 days indicated that fruit stored at low temperature had lower rate of increase in ethanol than fruit stored at room temperature.

Fruit respiration is as markedly affected by temperature in the physiological range as the respiration of any other plant tissue. Over the physiological range of most crops, e.g. 0 to 30°C (32 to 86°F), increased temperatures cause an exponential rise in respiration. The Van't Hoff Rule states that the velocity of a biological reaction increases 2 to 3-fold for every 10°C (18°F) rise in temperature (Saltveit, 1996). When oranges are stored at 3 and 5°C ethanol contents are the same whereas these content increased two times i.e., 90 mg/kg in samples kept under warm conditions (>20°C) (Hagenmaier, 2002).

Citrus are among the fruit that are sensitive to anaerobic conditions and storing them at low temperatures for long periods enhances the accumulation of acetaldehyde and ethanol (Pesis and Avissar, 1989). These experiments showed that tangerine fruit stored at low temperature, the amount of ethanol content in juice was less than fruit stored at ambient temperature. Low temperature could delay anaerobic respiration incidence. ‘Valencia’ oranges that were stored for 4 months at 6°C, the levels of ethanol and acetaldehyde were three times as high as in fruit stored at 6°C for 2 months and then at 17°C for an additional 2 months (Pesis and Avissar, 1989). No significant differences in ethanol accumulation of ‘Nova’ mandarins among coatings that included xanthan or locust bean gum, commercial formulation or non-coated fruit were detected during the first 30 days of storage at 5°C and 73% relative humidity (ethanol values ranged between 0 and 886 mg/l). Coatings that included guar gum or no hydrocolloid at all were inferior to others, with ethanol accumulation ranging from 2,196 to 2,249 mg/l (Chen and Nussinovitch, 2000a).

5.1.6 Fermentative enzymes : Pyruvate decarboxylase (PDC) and Alcohol dehydrogenase (ADH) activity

Effect of coating materials

The results showed that PDC activity of non-coated fruit was lower than PDC activity of coated fruit during storage at room temperature. It was also found that ADH activity of non-coated fruit was less than coated fruit through out the storage period. PDC and ADH activities of tangerine fruit coated with commercial coatings by commercial method and storage at 5°C were lower than storage at room temperature, and there was no difference from non-coated control fruit.

Both alcoholic fermentation and lactate fermentation occur during anaerobic metabolism in plants. The alcoholic fermentation pathway is more important for the survival of plant tissues under absence of O_2 (Dennis *et al*., 1997). The major function of this pathway is to regenerate NAD^+ from the glycolytic intermediate pyruvate, catalyzed by the enzymes PDC and ADH. Regeneration of NAD^+ is essential for plant tissues during anaerobic glycolysis in order to produce of some ATP through substrate-level phosphorylation, which permits the plant tissues to temporarily survive (Kader, 1995).

Severe stress concentrations of O_2 and/or CO_2 greatly inhibit cytochrome oxidase (CytOx) activity in fruit. NADH flux to the electron transport system is greatly reduced and oxidative phosphorylation is almost shut off. The dramatic decrease in ATP/ADP ratio releases the ATP control on ATP:phosphofructokinase (PFK) and activities of ATP:phosphofructokinase (PFK) and PPi:phosphofructokinase (PFP) increase to allow a greater carbon flux through glycolysis. Pyruvate dehydrogenase (PDH) activity may be reduced and pyruvate flux to the TCA cycle decreases. Under these conditions, PDC, ADH, and/or lactate dehydrogenase (LDH) are induced or activated to direct pyruvate to the anaerobic pathways (Ke *et al*., 1995).

Effect of storage temperatures

The results showed that tangerine fruit stored at 5°C had the highest ADH activity. However, no significant differences between tangerine fruit stored at 10°C and room temperature on ADH activity.

Not much has been reported in the literature about the effect of low temperature storage on fruit ADH activity. In tomatoes '7705' held at 20°C, ADH enzyme activity was maintained constant with respect to its initial levels during the whole storage period. At 10°C, a significant decrease in the activity of this enzyme was observed at 6 days with respect to the initial levels; after this point the enzyme activity was maintained constant until the end of the treatment and it was always lower than in fruit ripened at 20°C (de León-Sánchez *et al*., 2009).

5.1.7 Assessment of flavor and visual appearance

5.1.7.1 Flavor

Effect of coating materials

The flavor score of coated tangerine fruit decreased concurrently with the storage period, but differently depending on the treatments. Fruit coated with Zivdar had normal odor and taste, the same as control fruit during storage at room temperature.

Moreover, tangerine fruit coated with formulation A and Zivdar coatings noticeably reduced the flavor scores as compared with formulation B, C, D and control. The rapid decrease in flavor scores was noticeable for the tangerine fruit coated with formulation A after 7 days of storage. Unlike, the flavor score of the tangerines coated with formulation B, C and D which gradually declined. Formulation D coated fruit developed the smell and taste disorders later than other treatments, followed by fruit coated with formulation B, C and Zivdar. However, all the flavor scores of all coated fruit still acceptable, means that coated fruit had a little unusual flavor during storage.

Flavor can be adversely affected by the coating that reduces permeation of gases through the peel. Citrus fruit, like other plant products in general, continues to respire after harvest, intake O_2, and release CO_2. Unless these gases are able to pass through the peel without too much restriction, the CO_2 concentration builds up in the fruit and the O_2 becomes depleted. These changes can result in a change in the respiratory process so that off-flavor is produced (Hagenmaier, 1998a, b). Extremely low O_2 levels or excessively high CO_2 levels that induce fermentation can result in the generation of off-flavor (Cohen *et al*., 1990a, b). There was a relationship between the amounts of ethanol content and low O_2 and high CO_2 concentrations in tangerine fruit. The fruit coatings apparently reduced passage of O_2 through the peel and thus created partial anaerobic conditions in the fruit, which resulted in the formation of products of anaerobic respiration, e.g., ethanol and acetaldehyde. The coatings also prevented the exit of CO_2, ethanol, and acetaldehyde from the fruit, which led to fermentation and off-flavor induction (Cohen *et al*., 1990a, b; Mannheim and Soffer, 1996). Baldwin *et al*. (1995c) reported the marked increases in flavor volatiles, especially ethanol, ethyl butyrate, and ethyl acetate, in ‘Valencia’ oranges coated with a shellac-based citrus coating and stored at 16 to 21ºC. A high negative correlation between ethanol and flavor has also been reported for mandarin oranges (Ahmad and Khan, 1987) and 'Valencia' oranges (Ke and Kader, 1990).

Effect of storage temperatures

The result demonstrated that a better sensorial quality of tangerine fruit was found at 5 and 10°C than at room temperature. Coated tangerine fruit were stored under 5 and 10°C showed off-flavor and taste above the limit of marketability. When storage time was prolonged, a significant reduction in flavor scores was found, lower at room temperature than at 5 and 10°C.

In general, citrus fruit tends to develop off-flavor when stored at about 20°C after application of coating with low O_2 permeability that over restricted. The exchange of O_2 and CO_2 between atmosphere and fruit to the extent that internal O_2 concentration becomes too low to support aerobic respiration, with the result that ethanol, acetaldehyde, and other flavor components were produced (Hagenmaier and Baker, 1994b; Baldwin *et al*., 1995c; Hagenmaier, 2000, 2002). Tangerines are often coated in packinghouses with high-gloss coatings having low gas permeability (Amarante and Banks, 2001).

Hagenmaier (2002) study on coated citrus varieties with shellac-resin stored at 5°C for 7 days compared to citrus fruit coated with polyethylene-candelilla, polyethylene-shellac-candelilla, Britex 555 and shellac-resin. The results showed that citrus fruit coated with shellac-resin had stronger off-flavor and taste disorders. Coating 'Mor' mandarins with either of the two commercial waxes Tag and Zivdar and stored at 20°C for 7 days. It was found that flavor scores reduced from between 'good' and 'excellent' in control unwaxed fruit to 'fair' in wax-coated fruit (Tietel *et al*., 2010).

Off-flavor has been reported in citrus fruit with ethanol content of 3,100 mg/l for 'Temple' orange (Davis and Hofmann, 1973), ethanol > 2,900 mg/l for 'Murcott' tangerine (Cohen *et al*., 1990b), about 2,000 mg/l ethanol for 'Feutrell's Early' mandarin (Ahmad and Khan, 1987), above about 1,500 mg/l ethanol for 'Valencia' orange (Ke and Kader, 1990; Cohen *et al*., 1991), and more than about 1,500 mg/l for 'Temple' orange or tangor, the 'Dancy' tangerine, the 'Orlando' tangelo, the 'Nova' tangelo, the 'Robinson' tangerine, the 'Sunburst' tangerine, the 'Murcott' (or 'Honey') tangerine and the 'Fallglo' tangerine (Hagenmaier, 2002). Therefore, the ethanol contents of tangerine fruit coated with some coating give some concern about acceptability of their flavors.

Manolopoulou-Lambrinou and Papadopoulou (1995) reported that 'Encore' mandarins stored in the storehouse presented satisfactory taste after 10 days of storage. However, at the end of the 3rd week, they were inadequate in terms of taste. Mandarins preserved at 2 and 4°C maintained their flavor better. Fruit kept into storehouse maintained their flavor until the 10th day, but afterwards there was a significant decline of this parameter.

Under refrigerated conditions, flavor also deteriorates. 'Valencia' oranges stored at 3°C developed high ethanol and off-flavor after 10 weeks if coated, but not in polyvinyl chloride or left non-coated (Jimenez-Cuesta *et al*., 1983). The flavor of 'Clementine' decreased after 25 days at 4°C (Cuquerella-Cayuela *et al*., 1983). Ethanol content of 'Murcott' tangerines increased and flavor decreased after 4 weeks at 5°C for fruit with two coatings of wax (Cohen *et al*., 1991). Ethanol content of lemons, taken as an indicator of quality, increased markedly during storage at 2°C (Cohen *et al*., 1990a).

5.1.7.2 Visual appearance

Effect of coating materials

An appearance is the most important quality attribute of fresh produce with primary concern for size and color, uniformity, glossiness, and absence of defects in shape (Aked, 2000). Appearance can be affected by surface dehydration resulting in whitening, waxiness, and discoloration (like resulting from enzymatic browning). 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).

Tangerine fruit coated with commercial coatings showed better visual appearance results as compared with the non-coated control fruit. Data regarding storage intervals showed a gradual decline in appearance over the storage period prolonged. This may be the result of the loss of moisture, which in turn affected the quality of fruit. Water loss can cause shrinkage, softening of the flesh, ripening, senescence through ethylene production, and other metabolic changes (Bai *et al*., 2002).

The visual appearance of tangerines continuously decreased during storage, but the tangerines coated with coating materials were higher visual appearance score than non-coated control. Coating treatments imparted an attractive natural-looking sheen to the fruit. The results also showed that visual appearance scores depended on the type of coatings applied. Tangerine fruit coated with formulation A had the highest score, followed by fruit coated with formulation B, C, D and Zivdar. While, non-coated tangerine fruit had the lowest visual appearance score. Non-coated fruit begin to show clearly shrivel on the 5th day of storage and more shrivel on the 10th day of storage. For the coated fruit in all treatments began to show slightly shrivel about 8 days of storage.

The loss of commercial value of citrus fruit under various storage conditions is caused by transpiration, which lead to shriveling of the peel. Loss of water not only affects appearance or esthetic value but also reduces saleable weight, thus causing direct economic loss. Even 5-6% water loss can result in some change in appearance and firmness of the fruit that can be detrimental to its marketability (Ladaniya, 2008).

Wax coating is a special kind of operation in citrus fruit packinghouses since it accomplishes a triple objective: (1) protecting from water loss as coating replaces natural wax which is removed to some extent during washing operation, (2) providing the required gloss on which aesthetic value or cosmetic appearance of fruit depends, (3) acting as carrier for fungicide or any bio-gent and/or plant growth regulators such as 2, 4-D. Effective wax coating should reduce weight loss by about 30% (Hagenmaier and Baker, 2004).

Mandarin fruit coated with Britex, Decco, PacRite-Sunshine, Natural Zivdar, Zivdar PE, PacRite-StorRite and Primafresh was shiny and very attractive (Mannheim and Soffer, 1996). The gloss of oranges and grapefruit coated with wax was higher than that of uncoated fruit but lower than that of fruit coated with high-gloss commercial coatings (Hagenmaier and Baker, 1994b). 'Valencia' oranges coated with HIGLOSS coating (shellac and wood rosin) initially gave higher gloss than the wax coating (polyethylene-candelilla). However, this reversed after about 8 days of storage at 25°C, after which the oranges coated with polyethylene-candelilla wax coatings had better gloss (Hagenmaier, 2000).

Effect of storage temperatures

The results illustrated that tangerine fruit showed significantly less shriveling at 5 and 10°C compared with at room temperature. Temperature is the most important environmental factor that influences the deterioration of harvested commodities. The rate of deterioration of perishables however increases two to three-fold with every 10°C increase in temperature (Kader and Rolle, 2004).

Specific conditions are necessary for the storage of each citrus cultivar, as fresh fruit is likely to develop off-flavor, lose fresh appearance, and marketability. The set relative humidity and the temperature have to be uniform throughout the storage room and over the period of storage time. At higher temperature and lower relative humidity (66-65%) fruit exhibit higher transpiration rates, earlier senescence, and greater deterioration in visual appearance than fruits stored at lower temperature and higher humidity (90-95%) (Ladaniya, 2008).

5.1.8 Peel color

Effect of coating materials

Coating treatments had beneficial effects on the retardation of peel color changes during storage of tangerine fruit cv. 'Sai Nam Phueng'. Yellow color development was delayed by coating materials. During the storage period, hue angle values for both coated and non-coated tangerine fruit decreased significantly during storage period.

Hue angle, is a good estimate of color change from green to yellow color (McGuire, 1992). The hue angle decreases with the yellow pigments increases, showing the fruit peel turned to yellow-orange color. The loss of green color was the most obvious change in tangerine fruit, which was due to the degradation of the chlorophyll molecule and increased in carotenoid pigments during storage. The degradation was due to the oxidative system, pH change and enzymes like chlorophyllases (Wills *et al.*, 2007).

The main factors that retain peel color of tangerine fruit by coating materials are increased CO_2 levels and decreased O_2 levels which reduce respiration rate and delay ripening. The delay in ripening, degradation of chlorophyll and retention of green color for longer period also depend on types of coating materials (Manzano *et al*., 1997; Kittur *et al*., 2001), coating concentrations and temperature during storage (Carrillo *et al*., 2000; Malik *et al*., 2003).

Chen and Grant (1995) mentioned that wax was not effective on delayed yellowing of lemons, as compared to water control. Nature Seal®2020 half strength was more effective than storage wax and less effective than Nature Seal®2020 full strength. The greenest acid lime was found in fruit sealed with microperforated polyethylene bags after 10 weeks at 10°C (Ramin and Khoshbakhat, 2008). Peel yellowing of ‘Oroblanco’ fruit (*Citrus grandis* L. × *C. paradisi* Macf.) was reduced to a certain extent by individual sealing with perforated polyethylene liners or waxing with Zivdar water wax after 15-week storage, including 2 weeks at 1°C, 12 weeks at 11°C and 1 week at 20°C (Rodov *et al*., 2000). The treatment with 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) and waxing (Food-grade wax, Flucka AG, CH-9470 Buchs)) was more effective in delaying peel color development in ‘Balady’ limes during storage for 6 weeks at 18±1°C and 85-90% relative humidity (Ayoub and Abu-Goukh, 2009).

Effect of storage temperatures

Tangerine fruit stored at room temperature presented greater losses of green skin coloration as compared to those stored at 5°C, but was not significantly different from fruit stored at 10°C. Fruit stored at room temperature had the lowest hue angle values, and less green peel color.

Wills *et al.* (2007) mentioned that low storage temperatures decreased the rate of deterioration in non-climacteric commodities which retarded the degradation of chlorophyll. The lightness (L* value), intensity of color (chroma value) and hue angle of ‘Jewel’ strawberry fruit declined slightly during storage at 0.5°C, but decreased higher at 10 and 20°C (Shin *et al*., 2007). Jomori *et al*. (2003) reported that ‘Tahiti’ lime fruit kept at 10°C presented greater losses of green skin coloration compared to fruit stored at 5°C.

5.1.9 Total soluble solids (TSS)

Effect of coating materials

The results indicated that coating treatments had no effected on total soluble solids of tangerine fruit cv. 'Sai Nam Phueng' during storage. In addition, total soluble solids slightly increased during storage of both coated and non-coated tangerine fruit.

Several varieties of citrus fruit continue to accumulate soluble solids during storage (Purvis, 1983). In 'Hamlin' orange, for example, the increase in total soluble solids is accompanied by a parallel increase in sucrose and a concomitant decline in acid content (Echeverria and Ismail, 1987). The presence of all the gluconeogenic enzymes in mature sweet oranges suggests the possibility of de novo sugar synthesis from acid after the fruit is detached from the tree (Echeverria and Ismail, 1987). Thus, gluconeogenesis and *de novo* sugar synthesis do not seem to be involved in the second and final rise in Brix. Other varieties, such as 'Robinson' tangerine and 'Palestine' sweet lime do not show any direct correlation between the uninterrupted increase in Brix and changes in sugars after harvest (Echeverria and Ismail, 1987). In citrus, degradation of cellulose, hemicellulose, and pectin from cell walls of juice vesicles within fruit segments may release soluble components which could have a direct effect on Brix (Echeverria *et al*., 1988).

Application of Tag or Zivdar wax coatings did not cause any greater changes in juice total soluble solids levels of 'Mor' mandarins than those in unwaxed fruit held for 7 days at 20°C or stored for 3 or 6 weeks at 5°C plus 5 days under shelf life conditions at 20°C (Tietel *et al*., 2010). Luengwilai *et al*. (2007) reported that low O_2 atmospheres (1, 3, and 5 kPa) at 5°C for 8 weeks of storage had no effect on total soluble solids content of 'Clemenules Clementine' and 'W. Murcott' mandarins compared to the air control after being transferred to air at 20°C for 3 days of simulated marketing conditions. The total soluble solids of mandarin fruit were not affected by washing and sealing after the fruit were cured at 35°C with 95-98% relative humidity for 48 hours and stored at 5°C with 95% relative humidity for 30 days (Tariq *et al.*, 2001a). Shellie (2002) mentioned that 'Rio Red' grapefruit stored by reducing the O_2 concentration of the storage atmosphere from 21 to 0.10-0.05 kPa had similar concentration of total soluble solids as grapefruit stored in air.

Effect of storage temperatures

There was a significantly higher total soluble solids in fruit held at room temperature compared with 10 and 5°C. The slight increase in total soluble solids contents of tangerine fruit was measured during storage at 5, 10°C and room temperature for 43, 25 and 10 days, respectively.

This result agrees with the previously reported result for ‘Pineapple’ and ‘Valencia’ oranges during storage for 6 weeks at 4°C and 12 weeks at 1°C, respectively (Davis *et al*., 1973). Total soluble solids contents of ‘Hamlin’ oranges increased during stored at 15°C and 95% relative humidity for 4 weeks (Echeverria and Ismail, 1987). Burdon *et al*. (2007) stated that after 3 days of storage, ‘Satsuma’ mandarins stored at 30°C had higher total soluble solids compared with those stored at 18°C.

Tariq *et al*. (2001b) reported that total soluble solids of sweet oranges, ‘Satsuma’ mandarins and lemons were not affected by sealed in 120 gauge polyethylene bags after curing at 35°C with 95% relative humidity for 48 hours and subsequent storage at 5°C with 90% relative humidity for 28 days. The microperforation of polyethylene bags did not affect on soluble solid content of ‘Key’ acid lime fruit during storage for 10 weeks at 10°C and no significant differences were found among the type of microperforation bag (Ramin and Khoshbakhat, 2008). Soluble solid contents of ‘Valencia’ orange fruit was not affected significantly either by *trans* jojoba oil coatings or cold storage duration (Ahmed *et al*., 2007). Minimum changes of total soluble solids contents of ‘Valencia’ and local oranges of ‘Siavarz’ (*Citrus sinensis* L. Osbeck) were observed in wax treatments during stored in cold storage room (6±1°C and 75% relative humidity) (Ansari and Feridoon, 2007). Application of wax coatings (Tag and Zivdar) did not cause any greater change in juice total soluble solids levels of ‘Mor’ mandarin than those in unwaxed fruit held at 20°C for 7 days (Tietel *et al*., 2010).

5.1.10 Titratable acidity (TA)

Effect of coating materials

Titratable acidity of both coated and non-coated tangerine fruit cv. 'Sai Nam Phueng' also showed that no significant differences. There was a decrease in acidity in all treatments during storage.

Organic acids are an important source of acidic taste in fruit and also are respiratory substrates in the fruit. Organic acids are dissolved in cell sap either free or in combined form salts, esters, or glycosides. Juice from citrus fruits possesses a high content of organic acids, the highest being that of citric acid, followed by malic, succinic, adipinic, isocitric, a-ketoglutaric and aconitic acid. Most of the acid is probably present in the vacuole of the cell. (Murata, 1977a, b).

Respiratory quotient (CO_2 produced/O_2 consumed) which is higher (more than 1.00) indicates utilization of acids, mainly citric and malic acids through the tricarboxylic acid (TCA) cycle, in which acids are oxidized and ATP are formed for synthesis of new compounds. Organic acids are utilized during formation of many flavor and aromatic compounds (Ladaniya, 2008). The reduction of titratable acidity of tangerine fruit in all treatments may because of organic acids were used in the respiration, as a precursor of the respiration reactions or transformed into sugar to accumulation (Ball, 1997). Echeverria and Valich (1989) reported that 'Valencia' oranges, citrate is converted to other intermediates of the Krebs cycle, conversion of malic acid to pyruvate, production of ethanol, and conversion to sugars through gluconeogenesis.

No differences in acid concentrations were observed between waxed and seal-packaged 'Hamlin' oranges or 'Marsh' grapefruit stored at 21°C for 82 days or 'Marsh' grapefruit stored at 5°C (Purvis, 1983). There was no statistically significant difference in titratable acidity among 'Oroblanco' fruit (*Citrus grandis* L. × *C. paradisi* Macf.) individually sealed, or packed in cartons with perforated polyethylene liners, or waxed with Zivdar water wax after 15-week storage, including 2 weeks at 1°C, 12 weeks at 11°C and 1 week at 20°C (Rodov *et al*., 2000).

The use of solvent-based wax had no effect on the changes of acid in 'Valencia' oranges during stored at 10ºC (50°F) and 90% relative humidity for 4 weeks (Burns and Echeverria, 1990). In 'Valencia' and local oranges of 'Siavarz'

(*Citrus sinensis* L. Osbeck) cultivar, using of wax coating caused to inhibition of titratable acidity changes during stored at 6±1°C and 75% relative humidity (Ansari and Feridoon, 2007). The titratable acidity of 'Clemenules' mandarins treated with two commercial water-based waxes, both with the same wax composition (polyethylene wax and shellac) but two different total solids concentrations (70 and 100 g/kg) decreased with longer storage periods at 5ºC and 90% relative humidity for 12, 22, 32, 42, 52 or 62 days, plus 7 days at 20ºC to simulate shelf life marketing conditions (Marcilla *et al*., 2009). Tietel *et al*. (2010) reported that application of Tag and Zivdar waxes on ‘Mor’ mandarin did not cause any greater change in juice titratable acidity levels of than those in unwaxed fruit held at 20°C for 7 days.

Effect of storage temperatures

Tangerine fruit stored at 5, 10°C and room temperature for 43, 25 and 10 days, respectively, did not show significant differences in titratable acidity. A pattern of decreasing of the titratable acidity at the end of the shelf life was observed under all temperatures in comparison to the initial value.

The majority of the reduction in acids of citrus fruit was a decrease in citric acid (Burdon *et al*., 2007). Murata (1997) reported that the titratable acidity of ‘Satsuma’ mandarin juice, 85-90% of which consists of citric acid, declined approximately 13% over 4 weeks at 10°C compared with at harvest values, and postulated that the rate of turnover of citric acid is high during the storage period. Selselet-Attou (1977) mentioned that the temperature had no significant effect on acidity of mandarins Clementine cv. ‘Montreal’.

5.1.11 TSS/TA ratio

Effect of coating materials

There were no significant differences between coated and non-coated fruit in term of TSS/TA ratio. Moreover, the results showed that the TSS/TA ratio of all treatments was increased during storage. Similar results were found in Aloe vera-coated cherry and starch-coated strawberry (Martinez-Romero *et al*., 2006).

The decrease in acid concentration with a slightly increase or relative constant in total soluble solids contents resulted in increasing in the TSS/TA ratios of tangerine fruit during storage. These compositional changes with storage time may have a slight effect on taste due to lower acidity and sweetness. Ahmad *et al.* (1979) reported that waxing (3 or 6% Fruitex wax) and some lining materials (newspaper, 0.024 mm wax paper, cellophane or 0.030 mm polyethylene film) had no effect on the physico-chemical constituents of 'Feutrell's Early' mandarins. However, the sugar/ acid ratio increased during storage at 11-20°C. The brix-acid ratios of 'Marsh' grapefruit were not significantly different for fruit coated with high gloss shellac based coating, wax coating (12.0% polyethylene + 4.0% candelilla wax + 3.2% oleic acid, 0.8% myristic acid, and 0.9% NH_3, with 500 mg/kg thiabendazole) or non-coated control fruit (Hagenmaier *et al.*, 2002). Soluble solid contents (SSC) of 'Navel' oranges were increased by storage, while titratable acidity was decreased, leading to a progressive increase in the SSC/TA ratio as storage time. The SSC/TA ratios were not changed by process of commercially preparing fruit for market on a packing line by washing, grading, waxing and placement into boxes, and stored for 0, 3 or 6 weeks at 5°C followed by 4 days at 13°C and 3 days at 20°C (Obenland *et al.*, 2008).

Effect of storage temperatures

No significant differences in TSS/TA ratio were found among tangerine fruit stored at 5, 10°C and room temperature after 10 days of storage. Scholz *et al.* (1960) and Ke and Kader (1990) who observed similar concentration of TSS/TA ratio in 'Texas red' grapefruit stored in low O_2 (1-5 kPa) for 9 weeks at 5°C or in 'Valencia' oranges stored under 0.5, 0.25 or 0.02 kPa O_2 at 0, 5 or 10°C for 20 days, respectively. Luengwilai *et al.* (2007) reported that the decrease in titratable acidity was accompanied by no change in soluble solid contents, it resulted increase in TSS/TA ratio of 'Clemenules Clementine' and 'W. Murcott' juices, respectively, after kept in air or 5, 3 or 1 kPa for 8 weeks of 5°C followed by holding in air at 20°C for 3 days.

5.1.12 pH

Effect of coating materials

No difference was found among coating materials and non-coated in pH value of tangerine fruit. Comparison of treatment means showed an increasing trend of pH in all treatments during storage. The increase in pH may have been the result of the metabolisms of acids with respiration during storage (Togrul and Arslan, 2004).

The pH value was slightly increased during storage might be due to the formation of sugar and degradation of acids occur at higher storage temperature. The pH of tangerine juice in all treatments was increased as the titratable acidity was decreased.

Mandarins and tangerines like other citrus are harvested when fully ripe. The changes in their chemical constituents are, therefore, comparatively less than in the climacteric fruit where they are accelerated after picking and during ripening. Changes in the physicochemical constituents of citrus are influenced by seasonal variations, location, cultural practices, stage of maturity and postharvest storage conditions (Ahmad *et al*., 1979).

Ben-Yehoshua *et al*. (1979) mentioned that treatments like waxing or film lining have very little effect on pH value of mandarin fruit. The change of pH of coated and uncoated mandarins increased during storage for 27 days at 25°C and 75% relative humidity (Toğrul and Arslan, 2004). Ramin and Khoshbakhat (2008) mentioned that no significant differences were found on pH of ‘Key’ acid lime sealed with 40 microperforation high density polyethylene bag, 80 microperforation high density polyethylene bag, 120 microperforation high density polyethylene bag and no-polyethylene bag after stored for 10 weeks at 10°C.

Effect of storage temperatures

No significant differences in pH value of tangerine fruit were observed during storage at 5, 10°C and room temperatures. It was also found that the pH value showed a trend of decreasing during storage when held at 5, 10°C and room temperature.

Generally, the pH varies from about 2.0 for lemons and limes to about 4-4.5 in over-mature tangerines. The pH of the juice of ‘Valencia’ and ‘Washington’ navel oranges vary between 2.9 and 3.9. In ‘Palestine’ sweet limes, citric acid content of 0.08% was recorded with a pH 5.7 (Clements, 1964).

Ayala-Zavala *et al*. (2004) stated that no differences in pH of ‘Chandler’ strawberries among temperature treatments (0, 5 and 10°C) were observed.

Concellón *et al*. (2007) also reported that storage temperatures (0 and 10°C) had no effect on pH from pulp of eggplant during storage for 15 days.

5.1.13 Vitamin C

Effect of coating materials

Coating treatments had no effects on vitamin C contents of 'Sai Nam Phueng' tangerine fruit. The ascorbic acid or vitamin C content of coated tangerine fruit compared with non-coated control was not significantly different during storage. Moreover, the vitamin C contents of tangerine fruit in all treatments were quite variable during storage.

The approximate ranges for vitamin C of mandarins are 15-55 in tangerine, 20-60 in Mediterranean and 20-50 in Satsuma as mg/100 ml of juice. The vitamin C contents of most mandarin hybrids fall within the above ranges but some, for example, Temple (42-72 mg/100 ml), exceed these limits. The ascorbic acid contents of mandarins are generally lower than for oranges and grapefruit. In lemons and limes, vitamin C values show ranges of about 20-60 and about 15-45 mg/100 ml of juice, respectively (Nagy, 1980).

Toğrul and Arslan (2004) reported that no significant differences was observed in ascorbic acid contents for mandarin fruit coated with 18.5% paraffin wax + 5.3% emulgin polyethylene + 75.1% water + 1.1% carboxymethyl cellulose, 18.5% beeswax + 3.0% triethanolamine + 2.2% oleic acid + 75.2% water + 1.1% carboxymethyl cellulose, 8.8% soybean oil + 0.6% sodium oleate + 89.5% water + 1.1% carboxymethyl cellulose and control fruit during stored for 30 days at 25±1°C and 75% relative humidity. Verma and Dashora (2000) reported that ascorbic acid contents decreased for 'Kagzi' limes coated with mustard oil, neem oil, diphenyl, mustard oil + diphenyl, neem oil + diphenyl and control during kept at room temperature (24.6-32.8°C) for 12 days. Ascorbic acid of yellow passion fruit coated with Fruit wax, Sparcitrus, Sunny Side Citrus, and polyethylene was not significantly difference.

Effect of storage temperatures

Vitamin C contents of tangerine fruit coated with Zivdar, Fomesa, Citrashine by commercial method and non-coated fruit slightly decreased during storage at 5°C and room temperature but not significantly different among 5, 10°C and room temperature. When fresh citrus is stored at 3.3°C for 12 weeks, there was no loss of vitamin C, but when stored at higher temperatures, the loss was great (Nagy, 1980).

Ke and Kader (1990) reported that no significant difference in ascorbic acid contents of ‘Valencia’ orange between low-O_2 treatments and control fruit during storage at 5 or 10°C for 5, 9, 15, or 20 days followed by transfer to air at 5°C for 7 days. The amount of ascorbic acid in the juice of ‘Valencia’ oranges was no apparent effect due to the coating treatments after 1 month during storage at 16°C (Baldwin *et al*., 1995c). Manolopoulou-Lambrinou and Papadopoulou (1995) reported that temperature treatments did not affect the vitamin C content of ‘Encore’ mandarins which were stored into common storehouse as well as at 2, 4, 7 and 10°C with 90% relative humidity.

5.2 Correlation between study variables

The results showed that internal O_2 and CO_2 were both highly correlated with ethanol content. In addition, the results also showed that a negative correlation was found between internal O_2 and internal CO_2.

The regression analysis studies were undertaken to establish relationship between internal O_2, internal CO_2 and ethanol content of tangerine fruit. The relationship between internal O_2, internal CO_2 and ethanol content of tangerine fruit during storage were plotted and showed in Figure 4.61. The regression equations for the regressions of internal O_2 and internal CO_2 on ethanol content, and internal O_2 on internal CO_2 of ‘Sai Nam Phueng’ tangerines were as followed:

Internal O_2 versus ethanol content	$Y = -99.118x + 1740.6$
Internal CO_2 versus ethanol content	$Y = 152.16x - 544.61$
Internal O_2 versus internal CO_2	$Y = -0.5279x + 14.092$

The correlation coefficient (R) values for internal CO_2 was highly positive correlated with ethanol content ($R = 0.821$). The relationship between internal CO_2 and ethanol content or internal O_2 and internal CO_2 was highly positive. The relationship between internal O_2 and ethanol content or internal O_2 and internal CO_2 were negative.

Hagenmaier and Baker (1994b) reported that the relationship between ethanol and internal O_2 of 'Marsh' grapefruit was clearly non-linear. A similar relationship was found in 'Valencia' oranges. The CO_2 content, on the other hand, was almost linearly related with ethanol content. The ethanol content of the juice from coated 'Murcott' tangerine fruit showed an apparently linear correlation with the internal CO_2 of the fruit (Hagenmaier, 2001). Linear regression of ethanol against internal CO_2 in 'Valencia' oranges coated with polyethylene-candelilla coating after storage for 9 days at 25ºC gave a highly relation result (R = 0.943) (Hagenmaier, 2000). Hagenmaier (2000) also reported that because ethanol content increased with time and internal CO_2 did not, the regression parameters were dependent on storage time and temperature.

The relationship between internal gas and ethanol content is a function of storage time, since internal gases reach a steady-state level within a few hours, whereas ethanol increases with time (Hasegawa and Iba, 1980).

5.3 Scanning electron microscope (SEM) observation and permeability of coatings

5.3.1 Scanning electron microscope (SEM) observation

The epicuticular wax of 'Sai Nam Phueng' tangerine peel had a crystalline structure with high density of small platelets scattered on the surface and embedded in an amorphous wax layer and a number of round. Similar observations were made in fruit coated with formulation B and formulation C coatings, but lifted platelets were less pronounced than in non-coated fruit. Formulation A, D and Zivdar treatments, most platelets flattened and the skin surface appeared relatively homogeneous.

Wax is commercially applied to many fruit and vegetables to reduce dehydration and improve consumer appeal (Hall, 1981). The ability to reduce respiration and weight loss is affected most by storage temperature and then secondarily by the application of a wax coating.

Sala (2000) mentioned that the epicuticular wax of 'Fortune' mandarin peel had an amorphous structure in which crystalline plates and platelets were inserted. During fruit ripening, these plates separated from the wax layer, producing cracks and outer wax layer deficiencies (discontinuity in the outer layer of wax) caused by detachment of plates. Epicuticular wax damage increased during fruit ripening and the quantity of platelets decreased. At low temperature and relative humidity the epicuticular wax layer was more cracked and damage. Stomata were plugged and the wax layer around the stomata was more damaged, with cracks and wax deficiencies (Sala, 2000).

Ben-Yehoshua *et al.* (1985) reported that waxing with FMC$^{®5}$ solvent wax (coumarone indene resin, a polymerization product of crude heavy coal tar of naphtha) partially or completely plugs stomatal pores and forms an intermittent cracked layer over the surface of grapefruit (cvs. 'Marsh' and 'Duncan') and orange (cvs. 'Shamouti', 'Valencia' and 'Hamlin'). Scanning electron microscopy was used to examine the wax coating on 'Valencia' oranges. The natural wax platelets are irregular in shape and size, have a rough surface and increase in numbers as the orange matures. Store-bought oranges have natural wax platelets 1-2 microns thick covered with a 2-5 micron layer of commercial wax. Wax applied over platelets may be ineffective if the platelets break off in handling and expose the orange's surface. Removal of natural wax platelets prior to commercial waxing allows uniform wax application and consequently better storage life (Brusewitz and Singh, 1985).

Chen and Nussinovitch (2000b) also mentioned that coated 'Nova' mandarin with carnauba wax + xanthan gum formulations resulted in only partially blocked the stomata and created and more rugged, but non-uniform coating. The SEM study of the 'Clemantine' mandarin peel surface showed that cuticle is composed of high-density small crystalline epicuticular wax platelets embedded in an amorphous wax layer. On the other hand, this study also showed that 125 mg/l chitosan did not form a coating film, thus leaving the stomata uncovered the same as in the uncoated fruit (Fornes *et al.*, 2005).

5.3.2 Permeability of coatings

Polyethylene wax or oxidized polyethylene (OPE) or hydrocarbon wax, is permitted to use in the United States as a protective coating for fresh avocado, bananas, beets, coconuts, eggplant, garlic, mango, muskmelons, onions, papaya, peas (inpods), pineapple, plantain, pumpkin, rutabaga, squash (acorn), sweet potatoes, turnips, watermelon, Brazil nuts, chestnuts, filberts, hazelnuts, pecans, walnuts (all nuts in shells), grapefruit, limes, lemons, oranges and tangerines (CFR, 1990).

Polyethylene wax has the advantage of allowing the coated fruit to respire, thus avoiding the flavor changes that occur with less permeable coatings (Ben-Yehoshua, 1967; Davis and Hofmann, 1973). A number of polyethylene wax based coatings have been developed (Kaplan, 1986).

The measurements on permeability to gases and water vapor of wax are importance for fruit coatings. Permeability to water vapor is directly related to water loss of stored fruit. Permeability to O_2 and CO_2 governs the relationship between respiration and internal gas concentration and also importance to other gases, especially ethylene (Hagenmaier and Shaw, 1991a, b). Permeability for citrus coatings should be high for O_2, CO_2 and ethylene and low for water vapor to reduce transpiration as much as possible and not overly restrict respiration (Hagenmaier and Shaw, 1992).

5.3.2.1 Oxygen permeability

Film coated with 17.5% polyethylene microemulsion + 0.5% shellac micro-emulsion and Zivdar had permeance values lower than those of non-coated film. The results demonstrated that two coatings materials reduced the O_2 permeance about 12 and 16%, respectively, when compared with the control.

At 30°C and 40-80% relative humidity, shellac had permeability for O_2 and CO_2 for 230-700 and 800-5,800 cm^3/m^2-day, respectively. Under these conditions shellac is a better barrier to O_2 and CO_2 than cellulose acetate, polyethylene, polyethylene copolymer with vinyl acetate, polypropylene, polycarbonate, or polystyrene, but not as good a barrier as nylon 6, polyester or poly (vinylidene chloride) (Hagenmaier and Shaw, 1991b). The O_2 and CO_2 permeabilities of six polyethylene wax coatings at 30°C were 34,000 and 135,000 cm^3/m^2-day, respectively. In general coatings mad from polyethylene wax have values of O_2 and CO_2 permeability that are high compared to those of most other polymers (Hagenmaier and Shaw, 1991a). For the 19 commercials fruit wax coatings, the O_2 permeability at 30°C ranged from 470 to 22,000 cm^3/m^2-day. Permeability to non-condensable gases tended to be higher for coatings made from carnauba wax than those made from shellac and rosin (Hagenmaier and Shaw, 1992).

The transport coefficient of five gases, helium (He), argon (Ar), nitrogen (N_2), methane (CH4) and carbon dioxide (CO_2) were determined from permeation tests analysed by polymers, polyethylene (PE), polyamide 11 (PA11) and poly (vinylidene fluoride) (PVF_2), in a range of temperature from 40 to 80°C for PE and from 70 to 130°C for the others. For the diffusion and solubility coefficients, the polymer nature is obviously one of the most important parameters. Whatever the tested gas, polyethylene is more permeable than PA11 and PVF_2, which present a very similar behavior. This result is attributed to the high diffusion coefficients of gases in polyethylene. One explanation could be that the macromolecular chains of the amorphous phase of polyethylene have a greater mobility than those of the other materials (Flaconnèche *et al*., 2001).

5.3.2.2 Water vapor permeability

Under the condition of measurement, the water vapor permeance of coated and uncoated films showed slightly differences. Zivdar and 17.5% polyethylene microemulsion + 0.5% shellac microemulsion reduced the water vapor permeance about 8 and 6%, respectively.

Hagenmaier and Shaw (1991a) reported that for relative humidity not exceeding 50% at 30°C, the water vapor permeability of all shellac coatings was in the range 900-3,800 g/m^2-day. Shellac coatings cast from alcohol are better barriers to moisture vapor than cellulose, cellophane acetate, or nylon 6. However, they are poorer barriers to moisture vapor than polyester, polyethylene, polyethylene copolymer with vinyl acetate, polypropylene or poly (vinylidene chloride).

Six emulsions of polyethylene wax (oxidized polyethylene) were coated on highly permeable film. With oleic acid and morpholine used as emlsifiers, water vapor permeability of a high-density polyethylene wax coating was 1,700-3,200 g/m^2-day depending on the relative humidity gradient (Hagenmaier and Shaw, 1991b).