Stability of β -carotene in carrot powder and sugar confection as affected by resistant maltodextrin and octenyl succinate anhydride (OSA) starches

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Abstract Encapsulation has been used to overcome the problem of instability of functional pigments such as carotenoids from natural sources. In this study, β -carotene in carrot juice was spray dried with four different wall materials namely maltodextrin, resistant maltodextrin, octenyl succinate anhydride (OSA) starches Capsul (CAP) and HICAP-100 (HCAP). The objective of this research was to study the effects of various wall materials on physicochemical properties and stability of β -carotene powders along with its stability after incorporation into sugar confection. All four wall materials produced powders of acceptable quality in terms of moisture content, water activity, hygroscopicity, solubility as well as onset glass transition temperature. OSA starches exhibited better pigment retention post spray drying where juices encapsulated with HCAP showed the highest retention (94.34%). This was also represented in more orange Hue values (H°) in powders produced with CAP (53.93) and HCAP (53.33). Powders produced with HCAP also showed the longest half-life after storage at 4 °C, 25 °C, and 40 °C, as well as under exposure to light. Similarly, carrot powders produced with OSA starches also exhibited better β -carotene retention after production of hard candy confection. Though candies with HCAP encapsulated juices showed the highest β -carotene retention post candy processing, candies with CAP encapsulated carrot juices exhibited better long term

stability after storage at 25 °C and 40 °C as well as under exposure to light.

Keywords Encapsulation · Powder properties · Degradation kinetics · Confection · β -Carotene

Introduction

Carotenoids remain one of the largest groups of natural colorants available in nature. To date, more than 700 different carotenoid structures have been identified; however, only 50 are present within the human diet, with β -carotene, α -carotene, lycopene, lutein and cryptoxanthin making up 90% of the total carotenoid consumption (Rao and Rao 2007). Substantial literary evidence has proven that carotenoids are highly effective antioxidants (Paiva and Russell 1999). Certain carotenoids also serve a unique function as precursors to vitamin A, particularly β -carotene (Nagao 2004).

Carotenoids are highly sensitive to exposure to temperature, light, and oxygen. Encapsulation creates a protective barrier against these environmental factors by enveloping sensitive ingredients within a functional wall material. The most economically feasible method for encapsulation to date is the production of powders via spray drying (Desai and Park 2005). Among the important factors to consider during spray drying is the proper selection of the carrier or wall material, as it may affect the encapsulation efficiency (Gharsallaoui et al. 2007). Carbohydrate based carriers are increasingly being utilized due to the many variations of modified starches available on the market. Maltodextrins are the most commonly employed wall materials and are produced with various degrees of dextrose equivalents (DE). Resistant maltodextrins have

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also shown potential as wall materials in encapsulating probiotics (Lapsiri et al. 2012). Alternatively, new formulations for emulsifying starches have been produced by incorporating octenyl succinate anhydrate (OSA). These carriers may also serve an additional purpose as dietary fibres or slowly digested starches (Buck 2012).

β -carotene is widely incorporated into dairy products such as milk, yogurts and cheese. However, to the best of our knowledge there has been no report of β -carotene stability in confections whatsoever. The current research aims to study the effects of various wall materials, namely, maltodextrin DE 10 (MD), resistant maltodextrin (RMD), and the OSA starches CAPSUL® (CAP) and HI-CAP 100® (HCAP) on the physicochemical properties of spray dried carrot juices, their storage stability and the stability of these powders once incorporated into hard candy.

Materials and methods

Materials

Carrots of commercial maturity were obtained from a local market. Maltodextrin DE 10 (MD) and the resistant maltodextrin, Fibersol-2 (RMD) were obtained from San Soon Seng Food Industry, Malaysia and ADM Company, USA respectively. The modified starches CAPSUL (CAP) and HI-CAP 100 (HCAP) were purchased from Ingredion Malaysia SDN. BHD.

Chemicals

Sodium nitrate (NaNO_3), sodium azide (NaN_3), analytical grade solvents acetone ($\text{C}_3\text{H}_6\text{O}$), and N-hexane (C_6H_{14}), and HPLC grade solvents; methyl tert-butyl ether ($\text{C}_5\text{H}_{12}\text{O}$) and methanol (CH_3OH) were all obtained from Sigma Aldrich. Sodium chloride (NaCl) was purchased from Merck (Darmstadt, Germany).

Preparation of carrot powders

Carrots were washed, dried, and juiced with a Santos centrifugal juice extractor (*Vaulx-en-Velin*, France) to remove fibrous material. The juice was centrifuged, and the pellets were discarded. Carrot powders were produced through the method described by Muhammad et al. (2015) using a GAE Niro MOBILE MIRROR™ pilot scale spray dryer (GEA, Germany.) The juices were mixed with carriers at a 1:25 (w/w) ratio and homogenised with a Heidolph Silent Crusher M (Germany) at $280\times\text{g}$ for 10 min. Each aqueous feed was then spray dried at inlet and outlet temperatures of 150°C and 75°C , respectively, at an

atomisation rate of 15,000 rpm and feed rate of 10 mL/min. The spray dried powders were collected in aluminium laminated polyethylene (ALP) pouches, sealed, and stored at 4°C for further analysis.

Carrot powder properties

Determination of moisture content and water activity (a_w)

Moisture content was obtained by drying according to Loksuan (2007) while water activity was determined following the method by Fang and Bhandari (2011) using an Aqualab 3TE water activity meter (Pullman, USA).

Determination of percent hygroscopicity

Hygroscopicity was determined according to a method by Nayak and Rastogi (2010).

Determination of solubility

The cold water solubility of the powders was determined by diluting 0.5 g of powder in 50 mL distilled water. The mixture was then centrifuged at $3300\times\text{g}$ for 5 min. Subsequently 10 mL of the supernatant was transferred to a pre-weighted dish and oven dried at 105°C for 6 h. Percentage solubility was calculated according to the following formula:

$$\% \text{ Solubility} = \frac{W1 \times 5}{W0} \quad (1)$$

where W1, weight of solids in 10 mL and W0, weight of powder.

Determination of glass transition temperature (T_g)

The glass transition temperature was determined according to the method outlined by Fang and Bhandari (2012) using a Mettler Toledo 825e differential scanning calorimeter (DSC) (Germany).

Determination of average molecular weight of wall materials

Prior to chromatographic analysis, the refractive index increment (dn/dc) of each wall material was determined using a BI-DNDC differential refractometer (Brookhaven Instruments Corp., Holtsville, NY, USA). NaNO_3 solution (0.1 M) containing NaN_3 was used to dissolve the wall materials. NaN_3 was used as a preservative to prevent microbial growth. The average molecular weight was determined using high-performance size exclusion chromatography (HPSEC) coupled with multiple detectors: an

Agilent UV detector ($\lambda = 280$ nm), an Optilab rEX differential refractive index (RI) detector ($\lambda = 658$ nm), and a Dawn Heleos multi-angle laser light scattering (LS) detector ($\lambda = 661$ nm) (Wyatt Technology, Santa Barbara, CA, USA). The column used was a One PL aquagel-OH MIXED-H 8 μm column (Agilent Technologies, Santa Clara, CA, USA) with a resolving range of 100–10,000,000 g/mol. The mobile phase was composed of 0.1 M NaNO_3 solution containing NaN_3 (0.5 g/L). The flow rate used was 1.0 mL/min, and the analyses were performed at 25 °C. Samples were diluted with the mobile phase at 2.0 mg/mL and passed through 0.45 μm nylon filters prior to injection. Prior to measurement, the GPC-MALLS was validated against dextran standard (25 kDa). The output voltages from all detectors were collected and processed using the Wyatt Technology ASTRA V 5.3.4.14 program based on the first-order Zimm equation.

Determination of β -carotene retention

Extraction of carotenoids from carrot powder was conducted according to Desobry et al. (1997). Initially, 0.05 g of sample was dissolved in 1 mL of distilled water. Then, 1 mL of acetone and 4 mL of hexane were added before the mixture was stirred for 10 min and centrifuged at $3500 \times g$ for 5 min. The supernatant was then passed through a 0.45 μm nylon filter, and chromatographic determination was conducted according to Lessin et al. (1997) using a Waters Alliance 2986 HPLC system coupled with a UV/Vis detector and a YMC carotenoid C₃₀ column (5 μm particle size $\times$ 4.6 mm internal diameter $\times$ 150 mm length). The mobile phase used consisted of methanol:methyl tertbutyl ether at a ratio of 89:11 (v/v). Separation of carotenoids was achieved after 40 min at a flow rate of 0.7 mL/min. Detection was conducted at 410 nm. The retention of β -carotene was calculated according to the following formula:

$$\% \text{ Retention} = \frac{CC_f \times \%DM_p}{CC_p \times \%DM_f} \times 100 \quad (2)$$

where CC_f , peak area of β -carotene in feed; CC_p , peak area of β -carotene in powder; DM_f , dry mass of feed and DM_p , dry mass of powder.

Determination of colour

The colours of the powders were recorded using a Konica Minolta chromameter (Japan) based on L^* a^* b^* colour parameters. The hue angle (H°) and chroma (C^*) were calculated according to the following formulas:

$$H^\circ = \tan^{-1} \left(\frac{b^*}{a^*} \right) \quad \text{if } a < 0 \quad (3)$$

$$H^\circ = 180 - \tan^{-1} \left(\frac{b^*}{a^*} \right) \quad \text{if } a > 0 \quad (4)$$

$$C^* = (a^{*2} + b^{*2})^{\frac{1}{2}} \quad (5)$$

Determination of carrot powder morphology

The powder morphology was observed with an LEO 1455 VPSEM (United Kingdom) scanning electron microscope equipped with an Oxford INCA 300 energy-dispersive X-ray detector. Adhesive double-sided tape was attached to a metallic stub, and a small amount of powder was affixed to the tape, and coated with a thin layer of gold in a vacuumed evaporator. The sample was then viewed at 20 kV and magnitudes of $500\times$ and $700\times$.

Storage stability of carrot powder

Temperature and photostability

Temperature stability was assessed by storing 10 g lots of spray dried carrot powder sealed in ALP pouches under controlled conditions of 4 °C, 25 °C and 40 ± 3 °C for a period of 84 days (3 months). The β -carotene concentration was analysed every two weeks by HPLC.

Photostability was assessed by storing 10 g lots of each carrot powder sealed in clear plastic bags at 25 ± 3 °C; the samples were placed perpendicularly under illumination from an artificial light source: an 18 W 57 cm LED lamp that was elevated 50 cm above the samples for a duration of 4 weeks (28 days). Powders were analysed for β -carotene concentration every week. The kinetic degradation and half-life of β -carotene were calculated according to formulas (6) and (7), respectively.

$$\ln C_t = \ln C_0 - k_1 t \quad (6)$$

$$t_{1/2} = -\ln 0.5/k_1 \quad (7)$$

where C_t , pigment content after storage; C_0 , initial pigment content; t , storage time; k_1 , reaction rate constant for the first order model and $t_{1/2}$, half-life.

Storage stability of β -carotene in sugar confections containing carrot powder

Sugar confection formulation

The sugar confection or hard candy formulation was prepared according to our previous study (Shaaruddin et al. 2017). Briefly, sugar (64.5 g), corn syrup (45 g) and water

(15 g) were heated to 110 °C with continuous stirring. The mixture was then removed from the hot plate, carrot powder was added, and the mixture was stirred. The hot syrup was then poured into moulds and left to harden. After cooling, the candies were packaged in ALP pouches and stored at 4 °C until further analysis.

Stability of β -carotene in sugar confection containing carrot powder

The hard candies incorporated with carrot powders were sealed in 5 g lots in ALP pouches and stored for three months at temperatures of 25 °C and 40 °C for the temperature stability study. The storage and routine analysis of the hard candies for the photostability study of β -carotene were conducted similar to those applied for the powders. The retention of β -carotene post production of candy was calculated in comparison to the β -carotene in the spray dried powder, as calculated by Gu et al. (2015), while the retention of β -carotene during the storage of candies was calculated against the content at day zero.

Statistical analysis

Data were reported as the means $\pm$ standard deviations for triplicate analysis of two lots for each analysis. Minitab statistical software version 16 (State Collage, Philadelphia, USA) was used for one-way ANOVA, and Tukey's comparison test was used to determine significant differences among values. Statistical significance was determined at the level of $p < 0.05$.

Results and discussion

Carrot powder properties

The powder properties for the spray dried carrot powders are shown in Table 1. There were no significant differences in moisture content across powders with different wall materials except for RMD_c, which had a significantly higher content at 2.89%. Similarly, there was no significant difference in a_w values, which ranged from 0.24 to 0.35, well below the limit of 0.6 to be declared safe from microbial or mould spoilage (Ray and Bhunia 2007).

The percentage hygroscopicity of the wall materials and carrot powders exhibited a consistent pattern, in which the HCAP variants displayed the highest values followed by RMD, MD, and CAP. It can be noted that the carrot powders showed higher hygroscopicity than the initial wall materials. This result can be attributed to the sugars and organic acids present within the carrot juices. The HCAP variants may have exhibited more hygroscopic tendencies

due to the high dextrose equivalent (DE) of 32–37 of the wall material (Baranauskiene et al. 2007), indicating a large ratio of simple sugars (Bhandari et al. 1993) despite the high molecular weight of HCAP. This relationship was further confirmed by Soottitantawat et al. (2005), who stated that the incorporation of corn syrup solids occurs during the production of HCAP, causing an increase in its DE value and consequently increasing its hygroscopicity.

All spray dried carrot powders displayed high solubility characteristics ranging from 87 to 89%, with MD_c and RMD_c exhibiting slightly higher solubility than those containing OSA starches. This result is as expected, considering the presence of lipophilic functional groups in OSA starches. However, despite the more hydrophobic nature of OSA starches, Sweedman et al. (2013) reported that the incorporation of hydrophobic components within the starch backbone causes disruption in hydrogen bonding, allowing the starch chains to become more soluble. This behaviour explains why OSA starches still exhibit considerably good solubility characteristics. A clear decrease in solubility can be observed in the carrot powders compared to the initial wall materials. This decrease is probably due to the nature of the carrot juice, where the presence of non-polar compounds, including carotenoids, may hinder the solubilisation of the powder.

It can also be noted from Table 1 that HCAP_c showed the lowest T_g value, followed by CAP_c, MD_c, and RMD_c. OSA starches exhibited a significantly lower T_g than MD_c as well as significantly different values from one another. The T_g of RMD_c, however, did not differ significantly from that of CAP_c. The lower T_g values of OSA starches are likely because OSA functional groups also act as plasticizers, which are known to depress T_g values. This conclusion is supported by Silaket et al. (2014) who reported that higher degree of OSA substitution within the starch backbone reduces the onset glass transition temperature. Even so, CAP T_g values remained closer to that of RMD_c. This similarity could be ascribed to the retained native structure of CAP, which can be observed in Fig. 1, suggesting higher crystallinity than HCAP. Wijaya et al. (2011) also reported that CAP possessed a stronger crystalline pattern than HCAP. Increased crystallinity is associated with higher T_g . Furthermore, the addition of corn syrup solids to HCAP, as discussed previously, would have increased the fraction of simple sugars responsible for the depression of T_g . Nevertheless, the results indicated that all spray dried powders were storable at ambient temperatures. Storage below T_g ensures that the wall materials and carrot powders remain in their amorphous state which maintains the integrity of the core substance (Risch and Reineccius 1995). The average molecular weights of the wall materials from smallest to largest were in the order of MD, RMD, CAP and HCAP, in which MD and RMD differed only

Table 1 Properties of wall materials and carrot powders produced via spray drying with maltodextrin (MD), resistant maltodextrin (RMD), Capsule (CAP) and Hicap (HCAP)

	Wall material			
	MD	RMD	CAP	HCAP
Moisture (%)	3.71 ± 0.28 ^c	2.88 ± 0.25 ^d	7.74 ± 0.23 ^a	5.89 ± 0.05 ^b
Water activity (a_w)	0.47 ± 0.02 ^b	0.49 ± 0.02 ^b	0.57 ± 0.03 ^a	0.47 ± 0.00 ^b
Hygroscopicity (%)	8.75 ± 0.03 ^c	11.21 ± 0.03 ^b	8.25 ± 0.05 ^d	15.21 ± 0.08 ^a
Solubility (%)	91.81 ± 0.52 ^a	91.72 ± 0.44 ^a	90.62 ± 1.75 ^{ab}	87.45 ± 1.47 ^b
Glass transition (T_g)	65.19 ± 1.05 ^a	57.06 ± 0.06 ^b	58.35 ± 0.08 ^b	51.58 ± 0.12 ^c
Molecular weight (g/mol)	$3.531 \times 10^4 \pm 898.03^d$	$4.242 \times 10^4 \pm 1569.78^c$	$7.596 \times 10^4 \pm 808.10^b$	$1.595 \times 10^5 \pm 1555.63^a$
Chromatic measurement				
L	93.94 ± 0.29 ^b	93.96 ± 0.05 ^b	92.80 ± 0.13 ^c	95.49 ± 0.05 ^a
H°	100.84 ± 2.04 ^a	99.16 ± 0.93 ^a	91.38 ± 0.62 ^b	93.47 ± 1.36 ^b
C	1.35 ± 0.27 ^d	8.15 ± 0.11 ^b	9.61 ± 0.16 ^a	1.88 ± 0.08 ^c
	Carrot powders			
	MD _c	RMD _c	CAP _c	HCAP _c
Moisture (%)	2.08 ± 0.27 ^b	2.89 ± 0.07 ^a	2.18 ± 0.20 ^b	1.72 ± 0.25 ^b
Water activity (a_w)	0.35 ± 0.00 ^a	0.24 ± 0.01 ^a	0.32 ± 0.00 ^a	0.32 ± 0.01 ^a
Hygroscopicity (%)	13.36 ± 0.14 ^c	15.43 ± 0.17 ^b	12.60 ± 0.06 ^d	16.19 ± 0.09 ^a
Solubility (%)	89.43 ± 0.20 ^a	89.54 ± 1.23 ^a	88.43 ± 0.35 ^{ab}	87.03 ± 1.04 ^b
Glass Transition (T_g)	43.75 ± 0.26 ^a	44.35 ± 0.13 ^a	42.17 ± 0.04 ^b	39.89 ± 0.50 ^c
Chromatic measurement				
L	81.08 ± 0.02 ^a	79.98 ± 0.24 ^b	79.38 ± 0.03 ^c	80.16 ± 0.02 ^b
H°	56.72 ± 0.01 ^b	56.84 ± 0.02 ^a	53.93 ± 0.01 ^c	53.33 ± 0.02 ^d
C	30.53 ± 0.07 ^d	31.04 ± 0.02 ^c	34.54 ± 0.11 ^a	32.77 ± 0.18 ^b

Values are means ± standard deviations from triplicate analysis of two lots of each powder

Different superscript lettering within columns for each category indicates significant differences at $p < 0.05$

slightly. The higher molecular weight of both CAP and HCAP starches is most likely attributed to the incorporation of OSA into the starch backbone, in addition to the extensive branching amylopectin structure evident in waxy maize, which is the source starch for both CAP and HCAP.

Colour of carrot powders

The chromatic values of wall materials and carrot powders are shown in Table 1. The wall materials MD, RMD, CAP and HCAP were generally white in colour (91°–101° for H°), with HCAP being the brightest. The higher chroma for RMD and CAP was due to the slight yellowing of these wall materials.

Among the carrot powders, HCAP_c exhibited the most orange hue followed by CAP_c, MD_c and RMD_c, the carrot powders containing OSA starches showed a clear difference from those of MD_c and RMD_c. In terms of chroma, CAP_c exhibited the highest vividness in colour, followed by HCAP_c, RMD_c and MD_c. The higher chroma values of

CAP_c may be due to the initial yellowish tint of the wall material, as in the case of higher vividness in RMD_c than MD_c, even when the hue values suggested higher β-carotene contents in both HCAP_c and MD_c. Surface roughness may cause colour dilution as well as duller chroma even if samples possess higher contents of pigment compounds (β-carotene). This may explain why the hue and chroma values did not always coincide; the chroma values may be high, while the hue values may be low.

β-Carotene retention in carrot powders

Carrot powders containing OSA starches surpassed the performance of MD_c and RMD_c with CAP_c retaining slightly less β-carotene than HCAP_c. The retention of β-carotene in MD_c and RMD_c was 48.2% and 44.8%, respectively. This result could be caused by the lack of emulsifying characteristics of the wall materials. In contrast, the retention of β-carotene in CAP_c and HCAP_c was 80.76% and 94.34%, respectively. The well-known

Fig. 1 Wall materials, namely **a** maltodextrin, **b** resistant maltodextrin, **c** CAP and **d** HCAP, the morphology was observed with an LEO 1455 VPSEM scanning electron microscope equipped with an energy

dispersive X-ray detector. The wall materials were then viewed at 20 kV and magnitudes of 500 $\times$ and 700 $\times$

emulsifying characteristics of OSA starches are partly due to their high molecular weight, which allows these starches to form a thick layer at the oil/water interface. The long branching amylopectin backbone hinders the coalescence of droplets, thus increasing emulsion stability through steric hindrance (Dokić et al. 2012). This behaviour was supported by Sweedman et al. (2013), who reported that the higher molecular weight OSA starches tend to exhibit better emulsifying capacity. Higher β -carotene retention in HCAP_c might be due to the incorporation of corn syrup solids into the waxy maize base. The presence of low molecular weight sugars increases the flexibility of the film during encapsulation, resulting in a more thorough coverage of β -carotene. Liang et al. (2013) also reported higher concentrations of β -carotene in samples spray dried with HCAP than in those spray dried with CAP.

Carrot powder morphology

The granular structure of the spray dried powders was observed via scanning electron microscopy. Figure 1 shows the initial morphology of the as-received wall materials. In MD, RMD, and HCAP, the starch granules appeared damaged or fragmented, indicating extensive

modification of starch, primarily hydrolysis. However, CAP exhibited a distinctively more uniform and hexagonal shape, which suggests a lesser extent of hydrolysis, with its morphology leaning more towards that of native waxy corn starch. This observation is in line with the description by Paramita et al. (2012), who reported the DE of CAP to be 2, indicating minimal hydrolysis. The results also agreed with those of Rodríguez et al. (2013) who reported that although both CAP and HCAP are derived from waxy starch, only CAP retained its branching structure, while HCAP exhibited a more linear structure, denoting a higher extent of hydrolysis in the latter.

As shown in Fig. 2, the spray dried carrot powders have irregular forms with extensive dented surfaces, especially the MD_c and CAP_c samples. According to Rodríguez et al. (2013) this phenomenon is frequently observed in polysaccharide based wall materials. Teixeira et al. (2004) explained that surface indentation is influenced by the viscoelastic properties of the wall material as well as the drying rate. The carrot powders RMD_c and HCAP_c showed rounder and smoother granules, which could be attributed to the higher plasticizing attributes of the wall materials, as previously discussed. Additionally, Westergaard (2004) reported that the smoothing of particle surfaces is aided by

Fig. 2 Morphology of carrot juice spray dried with **a** maltodextrin, **b** resistant, maltodextrin, **c** CAP and **d** HCAP, observed with an LEO 1455 VPSEM scanning electron microscope equipped with an energy

dispersive X-ray detector. The wall materials were then viewed at 20 kV and magnitudes of 500 $\times$ and 700 $\times$

sugars present in the matrix. There have been several other accounts in which particles produced by HCAP yielded smoother and more rounded surfaces than CAP (Liang et al. 2013). This result is presumed to be caused by the presence of corn syrup in the HCAP formulation. The addition of sugars to modified starch is a common practice in order to increase the elasticity of encapsulated material.

Storage stability of β -carotene in carrot powders

The degradation of β -carotene in carrot powders was found to follow first order kinetics, as was reported in a previous study by Wagner and Warthesen (1995). In all samples, an increased rate constant (k) was observed, along with a corresponding decrease in half-life values ($t_{1/2}$), when the storage temperature was increased, as can be seen in Table 2. HCAP_c exhibited the highest stability among all spray dried samples, followed closely by CAP_c, before the stability reduced drastically for MD_c and finally RMD_c. The inferior stability in MD_c and RMD_c was most likely due to the low emulsification characteristics of the wall materials, leading to poor encapsulation and resulting in a higher surface content of β -carotenes. This configuration increases exposure towards oxidation and degradation. The higher pigment stability in HCAP_c than CAP_c may be

better understood by comparing the film properties of the two OSA starches. According to Liang et al. (2013), the oxygen permeability of films produced from CAP is significantly higher than that of films produced from HCAP, which is undesirable during the encapsulation of highly oxygen sensitive materials. Alternatively, the water vapour permeability of HCAP exceeded that of CAP, justifying highly hygroscopic nature of HCAP.

Carrot powders stored under illumination showed an increase in k values as well as a consequent drop in $t_{1/2}$ compared to powders stored at ambient temperature without light exposure. Carotenoid degradation is primarily in the form of isomerisation (Peseck and Warthesen 1990). Schieber and Carle (2005) reported that the conversion of a trans to cis species in carotenoids leads to reduced colour intensity. HCAP_c exhibited the highest $t_{1/2}$ followed in sequence by CAP_c, MD_c and RMD_c. The lower pigment retention in MD_c and RMD_c may be caused by a higher percentage of surface β -carotene due to poor encapsulation.

Retention of β -carotene in hard candy

Higher β -carotene retention was observed in candies with RMD_c than candies with MD_c. The retention was 64.81% and 68.42% for MD_c and RMD_c, respectively. This result

Table 2 Effect of storage temperature and light exposure on the degradation constant (k) and half-life ($t_{1/2}$) values of β -carotene in carrot powders and candies

	Temperature (°C)	k (weeks ⁻¹)	$t_{1/2}$ (weeks)
Carrot powders			
MD _c	4	0.0045	154.03
	25	0.0051	135.91
	40	0.0057	121.60
	Light	0.0205	34.66
RMD _c	4	0.0049	141.46
	25	0.0085	81.55
	40	0.0112	61.89
	Light	0.0187	32.74
CAP _c	4	0.0022	315.07
	25	0.0036	192.54
	40	0.0044	157.53
	Light	0.0110	63.01
HCAP _c	4	0.0016	433.22
	25	0.0018	385.08
	40	0.0029	239.02
	Light	0.0098	70.73
Candy incorporated with carrot powders			
MD _c	25	0.0308	22.50
	40	0.0726	9.55
	Light	0.0549	10.95
RMD _c	25	0.0322	21.53
	40	0.0880	7.88
	Light	0.0775	9.10
CAP _c	25	0.0114	60.80
	40	0.0417	16.62
	Light	0.0271	25.58
HCAP _c	25	0.0119	58.25
	40	0.0509	13.62
	Light	0.0279	24.84

MD, maltodextrin; RMD, resistant maltodextrin; CAP, Capsul; HCAP, Hicap

may be due to the protective effects of soluble fibres present in RMD. However, candies coloured with CAP_c and HCAP_c retained the highest percentage of β -carotene, with HCAP_c incorporated candies recording the highest retention of 82.71%, while CAP_c incorporated candies showed a retention of 73.26%. The lower retention of β -carotene in candies mixed with MD_c and RMD_c may be due to the smaller molecular weight of both of these wall materials than CAP and HCAP, which may reduce the thermal stability of the MD_c and RMD_c powders. Additionally, the lower initial content of β -carotene in the MD_c and RMD_c powders itself may have also resulted in lower retention post candy production. It must be noted, however, that

upon the addition of OSA starch encapsulated carrot powders to hot syrup, foaming occurred. This behaviour was more evident with CAP_c than HCAP_c. OSA starches possess high foaming characteristics (Kim et al. 2010). Starch esters have been widely used for their ability to stabilise foams and emulsions (Bhosale and Singhal 2007; Sweedman et al. 2013) and this characteristic most likely arises from their surface active properties. The higher retention of β -carotene in candies with HCAP_c may be due to the slightly lesser extent of foaming that occurs in HCAP than CAP. Furthermore, the larger molecular weight fractions present in HCAP may have provided additional heat protection for pigments.

Storage stability of β -carotene in hard candies

Candies incorporated with CAP_c and HCAP_c exhibited considerably lower degradation constants than candies with MD_c and RMD_c at both storage temperatures, as shown in Table 2. This result may be attributed to the higher pigment content of these two samples. Candies with HCAP_c exhibited higher degradation constants than candies with CAP_c despite the higher retention of β -carotene in the former candies post processing. This difference was more apparent after increasing the storage temperature. The higher stability of β -carotene in candies with MD_c was also observed compared to that in candies with RMD_c, despite the higher initial retention of β -carotene in candies with RMD_c.

The drastic drop in stability at 40 °C for all candies was most likely due to graining, which occurs in hard candy formulations when the amorphous matrix begins to crystallise unto itself. This crystallisation causes a breakdown of the glassy state and has been reported to reduce the stability of volatiles (Ergun et al. 2010). The results show that graining, accompanied by stickiness also reduced pigment stability in candies with carrot powder. Being high in sugar, hard candies are prone to becoming hygroscopic. Absorption of moisture from the surrounding environment may also contribute to graining and stickiness in glassy candies as it reduces T_g (Nowakowski and Hartel 2002). This behaviour further explains why candies with RMD and HCAP variants showed slightly poorer retention than candies with MD and CAP, respectively, due to their higher hygroscopic tendencies.

For candies stored under illumination, candies with OSA encapsulated carrot powder remained more stable than candies with MD_c or RMD_c. Exposure of β -carotene to light causes the all-trans species to convert to several different cis isomers (Pesek and Warthernsen 1990). This conversion leads to a noticeable reduction in colour intensity (Schieber and Carle 2005). The reduced stability of β -carotene in candies with MD_c and RMD_c might be due

to the initially lower pigment concentration in spray dried carrot powders. However, degradation caused by exposure to light was not as drastic as that caused by prolonged storage at 40 °C.

Conclusion

Carrot powders exhibited acceptable powder properties with all 4 wall materials. Despite this result, the concentration of β -carotene was drastically higher in carrot powders containing OSA starches, particularly HCAP (15.81 mg/100 g) which made it the most suitable preparation for spray dried carrot powder. Subsequently, HCAP_c continued to exhibit the highest β -carotene stability after storage. The incorporation of carrot powders in hard candy was successful, with the highest retention of 82.71% being observed for candies with HCAP_c. However, after storage, candies with CAP_c proved more stable, exhibiting the highest $t_{1/2}$ and lowest degradation rate constant. Pigment degradation caused by light and heat exposure suggests that carrot powders should be stored in chilled conditions while candies should be stored at room temperature with opaque packaging to ensure longer shelf life. Additionally, foaming which occurred in candies incorporated with carrot powders containing OSA starches, proved to be a processing hindrance, despite the acceptable stability of β -carotene exhibited by the carrot powder candies.

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