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Carbohydrate Polymers 50 (2002) 417–421

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Starch-based spherical aggregates: stability of a model flavouring compound, vanillin entrapped therein

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Received 24 July 2001; revised 6 March 2002; accepted 12 March 2002

Abstract

Studies on the stability of the vanillin entrapped within the spherical aggregates obtained from amaranth (*Amaranthus paniculatus* L.), quinoa (*Chenopodium quinoa* L.), rice (*Oryza sativa* L.) and colocasia (*Colocasia esculenta* L.) in the presence of gum Arabic, carboxymethyl cellulose (CMC) and carrageenan at 0.1–1.0% as bonding agents, were obtained by spray drying a 20% (w/w) starch dispersion at 120 °C. Vanillin was used at 5% based on starch (bos). The loss of vanillin over a 6-week storage period followed a first order kinetics. The stability was evaluated in terms of $t_{1/2}$ (weeks) from a semi-log plot of percentage retention of vanillin vs. storage time in weeks. The $t_{1/2}$ for the total vanillin and entrapped vanillin within the spherical aggregates prepared from different starches decreased in the order, amaranth > colocasia > chenopodium > rice. The $t_{1/2}$ decreased with an increase in the amylose content of the starches, although it was not linear. With respect to the bonding agent the stability decreased in the order, gum Arabic > CMC > carrageenan. While CMC and carrageenan gave an increasing value of $t_{1/2}$ with an increase in concentration from 0.5 to 1.0%, gum Arabic surprisingly gave a higher $t_{1/2}$ value at 0.5% as compared to 1.0%.

Keywords: Spherical aggregates; Entrapment of vanillin; Starches; Bonding agents; Stability

1. Introduction

Flavours are complex indispensable ingredients in food formulations that are also very sensitive to oxygen, heat and light. Encapsulation within matrices such as starches, hydrocolloids and various sugars have been used to protect such sensitive ingredients. The retention of these materials is governed by factors such as chemical nature of the core including the chemical functionality, relative volatility and polarity (Goubet, LeQuere, & Voilley, 1998). Controlled diffusion, breakage of the capsule, dissolution and solvent effects can cause loss of encapsulate. The degree of protection is generally calculated as the rate of its loss from the microcapsules. The ability of the carbohydrates to retain volatiles during drying processes makes them the most commonly used as coating materials (King, 1995; Shahidi & Han, 1993).

Recently, spherical aggregates prepared by spray drying of sensitive materials along with small sized starch granules in the presence of a carbohydrate or a protein-based bonding agent has been reported (Zhao & Whistler, 1994). These spherical aggregates, resembling popcorn balls, form porous interconnecting cavities that have the potential to hold large quantities of flavours for controlled release. Work from our laboratories demonstrated the role of amylose in the entrapment of a model flavour compound, vanillin in the spherical aggregates prepared from various small sized starch granules (Tari & Singhal, unpublished work). Among the various bonding agents tested for the suitability of entrapment, gum Arabic at 1.0% showed maximum retention of vanillin (Tari & Singhal, unpublished work). The present work reports on the degree of protection offered to vanillin by the spherical aggregates formed from various small sized starch granules during 6-week storage at room temperature.

2. Materials and methods

2.1. Materials

Twenty grams of starch, isolated from amaranth, colocasia, chenopodium and rice were dispersed in 80 ml water containing gum Arabic (0.1, 0.5 and 1.0%), carboxymethyl cellulose (CMC) (0.5 and 1.0%) and carrageenan (0.5 and 1.0%) as bonding agents individually. The slurry was stirred

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0144-8617/02/$ - see front matter
PII: S0144-8617(02)00055-3

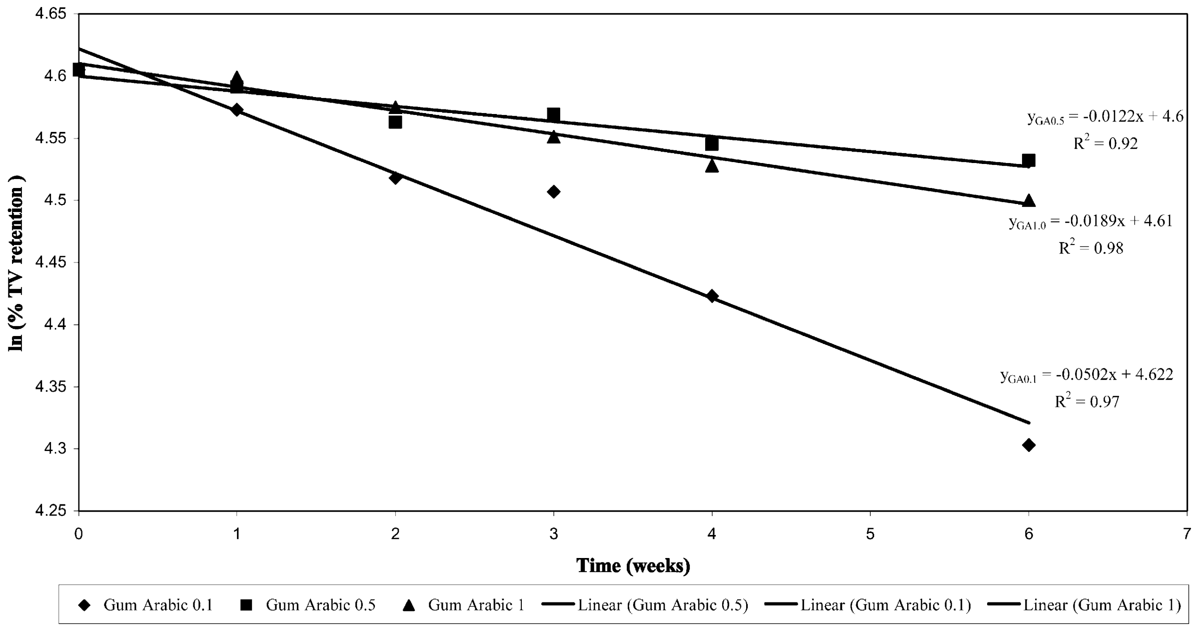

Fig. 1. Regression analysis of TV in the spherical aggregates using amaranth and gum Arabic as bonding agent.

for 5 min using a shear homogeniser to ensure uniform mixing. As vanillin is insoluble in water beyond 1%, it was first dissolved in minimum amount of propylene glycol and then the solution was mixed with the starch–polysaccharide mixture. This mixture was homogenised in a shear homogeniser for 5 min to ensure uniform distribution of vanillin in the network of starch–polysaccharide mixture. Vanillin was added at 5% based on starch (bos). The slurry containing all the components was spray dried in a Buchi-190 Model Mini Spray dryer (Buchi, Switzerland), (inside chamber dimension: 100 cm high, 60 cm diameter) equipped with 0.5 mm diameter nozzle. The pressure of compressed air for the flow of spray was adjusted to 5 bar. The inlet and outlet temperatures were maintained constant at 120 ± 2 and 76 ± 2 °C, respectively, to avoid gelatinisation of starch. A peristaltic pump was used to feed the spray dryer at 300 g/h. The spherical aggregates so prepared were collected from the collecting chamber. These powders were filled in airtight, self-sealable polyethylene pouches, and stored in a dessicator containing calcium chloride to prevent moisture absorption until further studies.

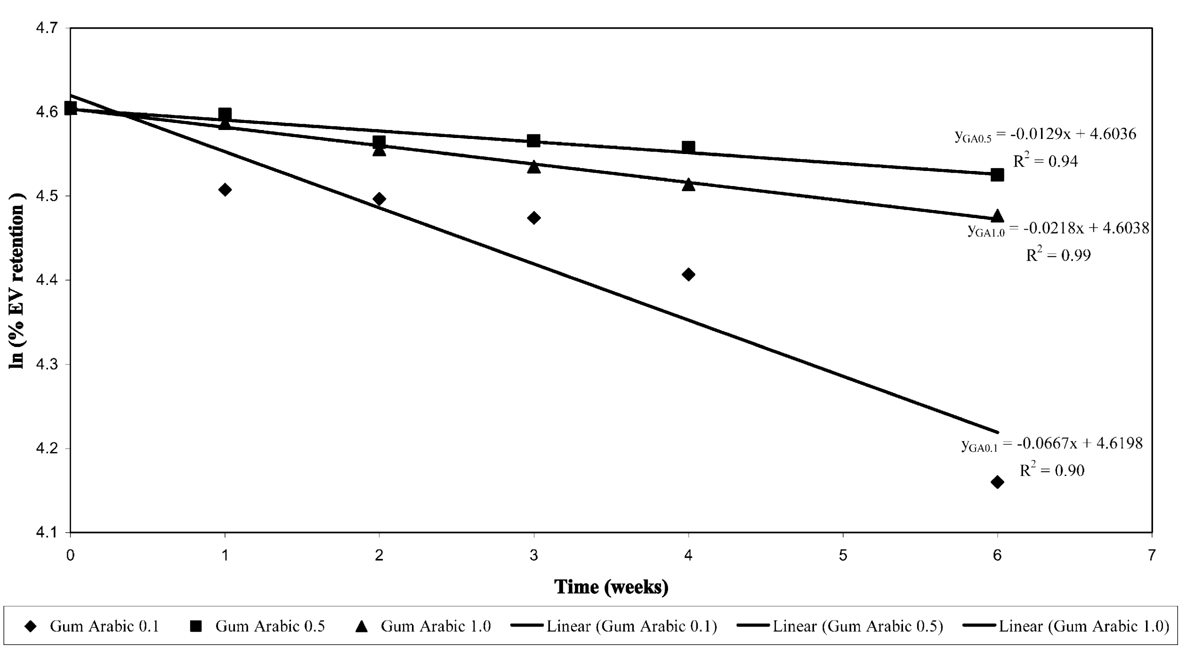

Fig. 2. Regression analysis of EV in the spherical aggregates using amaranth and gum Arabic as bonding agent.

Table 1
Regression analysis of TV in the spherical aggregates with time of the starches under study (vanillin at 5% bos; values within parenthesis indicate the correlation coefficient)

Binding agents (%)	Amaranth	Colocasia	Chenopodium	Rice
Gum Arabic at 0.1%	$Y = -0.0502x + 4.622$ ($R^2 = 0.97$)	$Y = -0.0927x + 4.5707$ ($R^2 = 0.96$)	$Y = -0.1131x + 4.5627$ ($R^2 = 0.98$)	$Y = -0.0803x + 4.5647$ ($R^2 = 0.92$)
Gum Arabic at 0.5%	$Y = -0.0122x + 4.6$ ($R^2 = 0.92$)	$Y = -0.0352x + 4.5971$ ($R^2 = 0.97$)	$Y = -0.0478x + 4.5847$ ($R^2 = 0.93$)	$Y = -0.0655x + 4.6041$ ($R^2 = 0.95$)
Gum Arabic at 1.0%	$Y = -0.0189x + 4.61$ ($R^2 = 0.98$)	$Y = -0.0365x + 4.5891$ ($R^2 = 0.96$)	$Y = -0.0541x + 4.5946$ ($R^2 = 0.97$)	$Y = -0.0747x + 4.6037$ ($R^2 = 0.97$)
CMC at 0.5%	$Y = -0.0507x + 4.6066$ ($R^2 = 0.99$)	$Y = -0.0435x + 4.5712$ ($R^2 = 0.90$)	$Y = -0.0597x + 4.5957$ ($R^2 = 0.99$)	$Y = -0.0818x + 4.5727$ ($R^2 = 0.98$)
CMC at 1.0%	$Y = -0.0497x + 4.5828$ ($R^2 = 0.95$)	$Y = -0.049x + 4.5781$ ($R^2 = 0.97$)	$Y = -0.0577x + 4.5656$ ($R^2 = 0.95$)	$Y = -0.0735x + 4.583$ ($R^2 = 0.97$)
Carrageenan at 0.5%	$Y = -0.0708x + 4.5987$ ($R^2 = 0.97$)	$Y = -0.0906x + 4.5783$ ($R^2 = 0.96$)	$Y = -0.1022x + 4.5643$ ($R^2 = 0.96$)	$Y = -0.1527x + 4.5967$ ($R^2 = 0.99$)
Carrageenan at 1.0%	$Y = -0.0554x + 4.5968$ ($R^2 = 0.97$)	$Y = -0.0651x + 4.5897$ ($R^2 = 0.96$)	$Y = -0.0926x + 4.6015$ ($R^2 = 0.97$)	$Y = -0.1676x + 4.6208$ ($R^2 = 0.99$)

Table 2
Regression analysis of EV in the spherical aggregates with time of the starches under study (vanillin at 5%, bos; values within parenthesis indicate the correlation coefficient)

Binding agents (%)	Amaranth	Colocasia	Chenopodium	Rice
Gum Arabic at 0.1%	$Y = -0.0667x + 4.6198$ ($R^2 = 0.90$)	$Y = -0.1526x + 4.6537$ ($R^2 = 0.98$)	$Y = -0.1636x + 4.6578$ ($R^2 = 0.98$)	$Y = -0.1458x + 4.6741$ ($R^2 = 0.98$)
Gum Arabic at 0.5%	$Y = -0.0129x + 4.6036$ ($R^2 = 0.94$)	$Y = -0.0571x + 4.605$ ($R^2 = 0.99$)	$Y = -0.0603x + 4.6177$ ($R^2 = 0.99$)	$Y = -0.0607x + 4.6274$ ($R^2 = 0.98$)
Gum Arabic at 1.0%	$Y = -0.0218x + 4.6038$ ($R^2 = 0.99$)	$Y = -0.0367x + 4.6161$ ($R^2 = 0.99$)	$Y = -0.0604x + 4.6297$ ($R^2 = 0.98$)	$Y = -0.0881x + 4.6313$ ($R^2 = 0.99$)
CMC at 0.5%	$Y = -0.0971x + 4.6425$ ($R^2 = 0.98$)	$Y = -0.0456x + 4.6072$ ($R^2 = 0.98$)	$Y = -0.0809x + 4.6342$ ($R^2 = 0.99$)	$Y = -0.1255x + 4.6581$ ($R^2 = 0.98$)
CMC at 1.0%	$Y = -0.0858x + 4.6162$ ($R^2 = 0.97$)	$Y = -0.0384x + 4.6163$ ($R^2 = 0.97$)	$Y = -0.0722x + 4.6151$ ($R^2 = 0.98$)	$Y = -0.0911x + 4.6342$ ($R^2 = 0.98$)
Carrageenan at 0.5%	$Y = -0.1245x + 4.6279$ ($R^2 = 0.99$)	$Y = -0.1176x + 4.612$ ($R^2 = 0.99$)	$Y = -0.1815x + 4.6884$ ($R^2 = 0.97$)	$Y = -0.2035x + 4.7162$ ($R^2 = 0.96$)
Carrageenan at 1.0%	$Y = -0.1124x + 4.662$ ($R^2 = 0.96$)	$Y = -0.0951x + 4.646$ ($R^2 = 0.98$)	$Y = -0.1082x + 4.6413$ ($R^2 = 0.98$)	$Y = -0.1574x + 4.6857$ ($R^2 = 0.97$)

2.2. Methods

2.2.1. Stability of the TV and EV within the spherical aggregates

The samples were analysed every week for 6 weeks for total vanillin (TV) and entrapped vanillin (EV) by the method described by North (1949). The percentage retention of TV and EV was calculated by the formula: [(vanillin at X storage time) $\times$ 100/(vanillin at zero storage time)]. A semi-log plot of percentage retention of TV and EV vs. time according to Cai and Corke (2000) was done to obtain the rate constant (k) as the slope of the graph. Half-life ($t_{1/2}$) for the retention of vanillin was calculated from the rate constant as $0.693/k$.

3. Results and discussion

The starches in this study had been previously evaluated to contain 2.5% amylose in amaranth starch, 17.5% in colocasia starch, 22.5% in quinoa starch and finally 39% in the rice starch (Tari & Singhal, unpublished work). The results of TV and EV in the spherical aggregates prepared from amaranth, colocasia, chenopodium and rice starches using gum Arabic (0.1, 0.5 and 1.0%), CMC (0.5 and 1.0%) and carrageenan (0.5 and 1.0%) over a 6-week storage period were evaluated. In all cases, both TV and EV declined during storage. In order to study the stability of TV and EV within the aggregates, a semi-log plot of percentage retention of vanillin vs. time was plotted for each sample of starch type and bonding agent. Linear graphs were obtained in all cases, indicating a first order kinetics of the same. Fig. 1 shows one such graph wherein ln (percentage retention of TV) vs. storage time is shown with spherical aggregates of amaranth starch with gum Arabic at 0.1, 0.5 and 1.0% as the bonding agents. The slopes of the regression equation gives the rate constant, k, from which the half-life, $t_{1/2}$ was calculated as $0.693/k$. The regression analysis

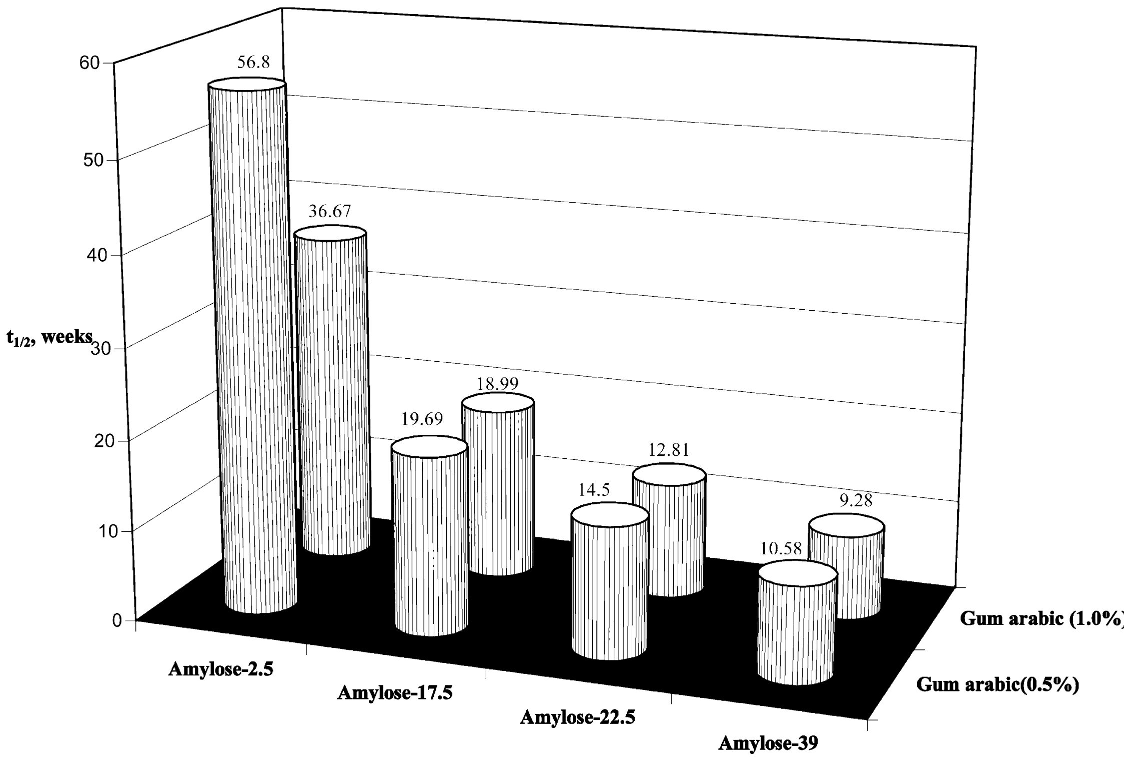

Fig. 3. Effect of amylose content on $t_{1/2}$ of TV in spherical aggregates using gum Arabic as bonding agent.

performed for all the experimental samples is compiled in Table 1. Similarly, Fig. 2 shows similar data on ln (percentage retention of EV) vs. storage time for amaranth starch with gum Arabic as the bonding agent. In this case also, the linear nature of the graph confirmed a first order kinetics for the loss of EV from the spherical aggregates. Table 2 compiles the regression analysis of ln (percentage retention of EV) vs. time for all the experimental samples.

Table 3 shows the half-life of TV and EV in all the experimental samples. A close look at this table indicates amaranth starch with gum Arabic at 0.5% to have a maximum half-life of 56.80 weeks for TV and 53.72 weeks for EV. The spherical aggregates for all starches had lower $t_{1/2}$ for the stability of vanillin when carrageenan and CMC were used as the bonding agents. Among the two, CMC had a slightly better effect than carrageenan. Further, this half- life does seem to have some correlation with amylose content, although not a linear one. This is shown in Fig. 3, which shows the half-life of TV for the spherical aggregates prepared from the experimental starches using gum Arabic at 0.5 and 1.0%. Similar graph was obtained for EV (figure not given).

The role of amylose in the starches used for preparing the spherical aggregates for holding food constituents and its stability, such as in this case, vanillin need to be studied in depth. The reasons for gum Arabic giving maximum

Table 3
Half-life ($t_{1/2}$) in weeks of spherical aggregates of starches under study using estimation of TV and EV (vanillin at 5% bos)

Binding agents (%)	$t_{1/2}$ (weeks)							
	Amaranth		Colocasia		Chenopodium		Rice	
	EV	TV	EV	TV	EV	TV	EV	TV
Gum Arabic (0.1%)	10.39	13.80	4.54	7.48	4.34	6.13	4.75	8.63
Gum Arabic (0.5%)	53.72	56.80	12.14	19.69	11.49	14.50	11.42	10.58
Gum Arabic (1.0%)	31.79	36.67	18.88	18.99	11.47	12.81	7.87	9.28
CMC (0.5%)	7.14	13.67	15.20	15.93	8.57	11.61	5.52	8.47
CMC (1.0%)	8.08	13.94	18.05	14.14	9.60	12.01	7.61	9.43
Carrageenan (0.5%)	5.57	9.79	5.89	7.65	3.82	6.78	3.41	4.54
Carrageenan (1.0%)	6.17	12.51	7.29	10.65	6.40	7.48	4.40	4.13

stability as compared to CMC and carrageenan is also an area of investigation. Evaluation of polysaccharide combinations or protein-based bonding agents on the stability of the entrapped constituents also warrants attention. This work also needs to be done with flavour compositions containing a multitude of chemically distinct components to know whether the observations are specific to vanillin, or independent of the entrapped molecule.

References

Cai, Y. Z., & Corke, H. (2000). Production and properties of spray-dried *Amaranthus* betacyanins pigments. *Journal of Food Science*, *65*, 1248–1252.

Goubet, I., LeQuere, J. L., & Voilley, A. J. (1998). Retention of aroma compounds by carbohydrates: Influence of their physicochemical characteristics and their physical state—a review. *Journal of Agricultural and Food Chemistry*, *46*, 1981–1990.

King, A. K. (1995). Encapsulation of food ingredients: A review of available technology, focusing on hydrocolloids. In S. J. Risch & G. A. Reineccius, *Encapsulation and controlled release of food ingredients* (pp. 26–41). Washington, DC: American Chemical Society.

North, H. (1949). Colorimetric determination of capsaicin in oleoresin of capsicum. *Analytical Chemistry*, *21*, 934–936.

Shahidi, F., & Han, X. Q. (1993). Encapsulation of food ingredients. *CRC Critical Reviews in Food Science and Nutrition.*, *33*, 501–547.

Zhao, J., & Whistler, R. L. (1994). Spherical aggregates of starch granules as flavour carriers. *Food Technology*, *48 (7)*, 104–105.