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Starch based spherical aggregates: reconfirmation of the role of amylose on the stability of a model flavouring compound, vanillin

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Abstract

The stability of the total vanillin (TV) and entrapped vanillin (EV) within the spherical aggregates prepared from various starches over a 6-week storage period appeared to be correlated to the amylose content of the starches, in a previously conducted study. To reconfirm this observation, spherical aggregates were prepared from amaranth starch (containing 2.5% amylose), and from blends of amylose and amaranth starch (in ratios of 10:90, 20:80, 30:70 and 40:60 ratios) of vanillin (used at 5% based on starch) using gum Arabic at 1.0% as the bonding agent. The loss of TV and EV from the spherical aggregates followed a first order kinetics, from which the stability was evaluated in terms of $t_{1/2}$, the time required for TV or EV to decrease to 50% of its original value. The $t_{1/2}$ for the TV and EV within the spherical aggregates so prepared were evaluated as a function of the added amylose. The $t_{1/2}$ for TV remained almost unchanged with amylose up to 20%, thereafter decreased substantially at 30%, and very sharply at 40%. With EV, the decrease in $t_{1/2}$ was less up to 30% amylose in the blend, but decreased very sharply at 40% amylose. These results confirm our earlier observation of the role of amylose on the stability of EV and TV within the spherical aggregates. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Spherical aggregates; Amaranth starch/amylose blend; Gum Arabic; Bonding agent; Entrapped vanillin

1. Introduction

Encapsulation of complex ingredients that are sensitive to light, heat and oxygen within matrices such as starches, hydrocolloids and various sugars have been used in food processing for a long time. The ability of the carbohydrates to retain volatiles during drying processes makes them the most commonly used coating materials (King, 1995; Shahidi & Han, 1993).

Factors such as chemical nature of the core, chemical functionality and polarity govern the retention of these materials within the microcapsules (Goubet, LeQuere, & Voilley, 1998). The encapsulate can be lost from the microcapsules by mechanisms such as controlled diffusion, breakage of the capsule, dissolution and solvent effects. The degree of protection is generally calculated as the rate of its loss from the microcapsules.

Recently, spherical aggregates, resembling popcorn balls, 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). The conditions of spray drying are selected so as to prevent the gelatinization of the starch. These spherical aggregates form porous interconnecting cavities capable of holding large quantities of flavours for controlled release. Previous communication from our laboratories indicated the role of amylose, not only on the entrapment of a model flavour compound, vanillin in the spherical aggregates prepared from various small sized starch granules, but also on its stability (Tari and Singhal, unpublished work). The present work seeks to reconfirm the role of amylose on the stability of vanillin within spherical aggregates prepared from amaranth starch, and that obtained by blending up to 40% amylose to amaranth starch that was shown to contain 2.5% amylose in our previous report (Tari and Singhal, unpublished work). Vanillin within the spherical aggregates is termed as 'entrapped vanillin (EV)', while the sum total of entrapped and surface vanillin is referred to as 'total vanillin (TV)' through out this work.

2. Materials and methods

2.1. Materials

Amaranth starch was isolated by the alkali steeping method as described by Yanez and Walker (1986). Standard

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Table 1
Recovery of vanillin (%) (vanillin at 5% bos) in spherical aggregates prepared from blend of amaranth starch and amylose (results are mean of two individual determinations)

Amylose content (%)	Recovery of vanillin (%)											
	0 week		1 week		2 weeks		3 weeks		4 weeks		6 weeks	
	EV	TV	EV	TV	EV	TV	EV	TV	EV	TV	EV	TV
0	83.0	94.0	81.5	92.5	79.0	89.5	77.4	85.5	75.8	85.0	73.0	84.0
10	66.6	82.0	65.2	79.9	62.5	78.0	61.0	76.0	59.2	74.5	57.8	73.5
20	63.4	79.0	61.4	77.4	59.6	74.5	58.4	73.0	57.2	72.0	54.0	71.5
30	58.2	74.0	54.8	73.2	54.5	69.33	53.2	67.5	50.7	66.5	48.0	65.0
40	54.5	72.0	48.2	67.4	44.6	61.65	38.2	58.61	37.2	55.5	27.8	54.0

amylose was procured from M/s Sigma Chemical Co., USA, while gum Arabic was obtained from M/s Drytech Processes India Pvt. Ltd, Mumbai, India.

2.2. Methods

2.2.1. Preparation of the spherical aggregates

Spherical aggregates of small sized starch granules from amaranth (*Amaranthus paniculatus* L.), using 1.0% gum Arabic as the bonding agents were prepared by spray drying a 20% (w/w) starch dispersion containing vanillin at 5% based on starch (bos) using 120 ± 2 and 76 ± 2 °C as the inlet and outlet temperature, respectively. Other conditions were similar as that described in our previous communications (Tari and Singhal, 2002). Amylose was added to amaranth starch at 0–40% and spherical aggregates prepared similarly. All the samples were packed in self-sealable polyethylene bags and stored at room temperature in a desiccator until analysis.

2.2.2. Analysis for the TV and EV within the spherical aggregates

The samples were analyzed every week for 6 weeks for TV and EV as follows: 0.25 g of spherical aggregates were washed with 25 ml of absolute alcohol and the filtrate made to 50 ml in a volumetric flask with distilled water. This was filtered using Whatman No. 1 filter paper to remove the surface vanillin. The residue was dissolved in distilled water, volume made to 100 ml in a standard volumetric flask, and used to estimate EV using 1 ml aliquot by the procedure of North (1949). The total time required for washing with alcohol, filtration, and making solutions, both in alcohol and water for estimation of surface and entrapped vanillin, respectively, were approximately 1 h. Losses of

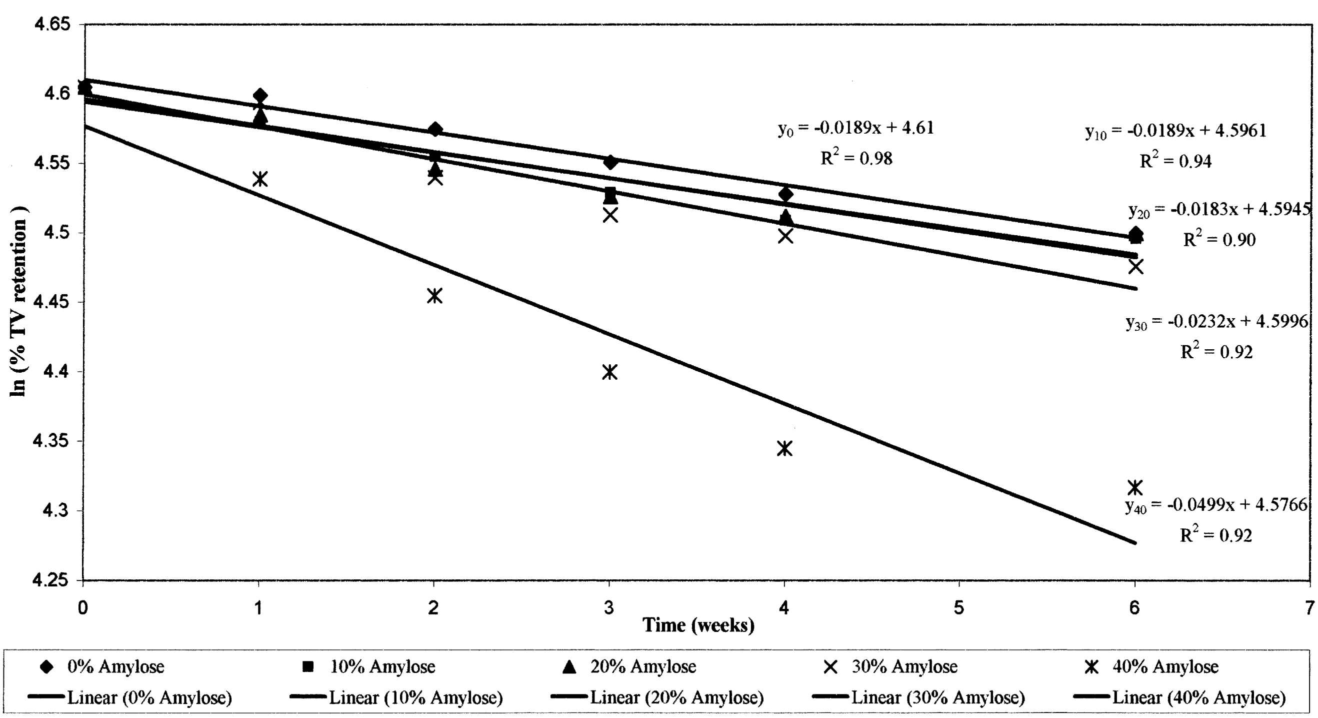

Fig. 1. Regression analysis of TV in the spherical aggregates using amaranth starch/amylose blend and 1.0% gum Arabic as bonding agent.

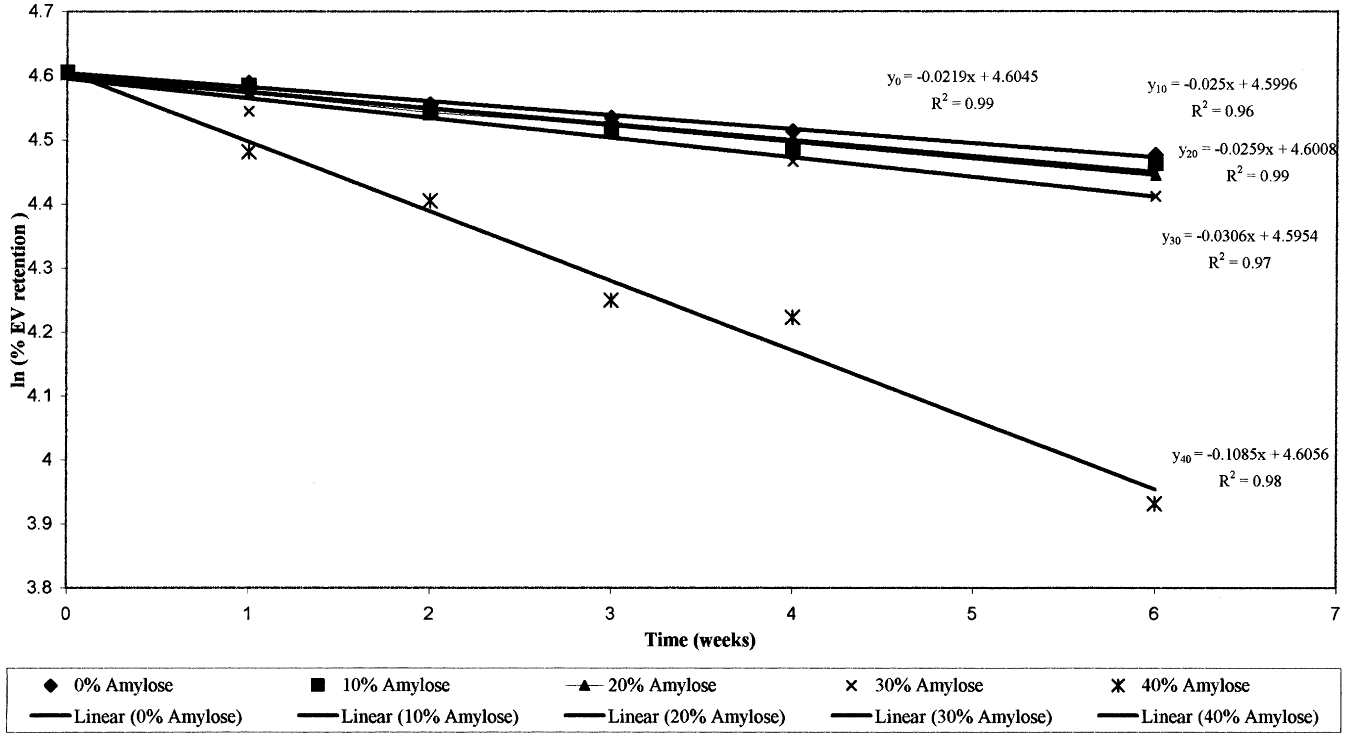

Fig. 2. Regression analysis of EV in the spherical aggregates using amaranth starch/amylose blend and 1% gum arabic as the bonding agent.

vanillin occurred during this period. Hence, TV was estimated after dissolving 0.1 g of spray-dried spherical aggregates in 100 ml distilled water in a standard volumetric flask. Vanillin was estimated in 1 ml of each sample (North, 1949).

2.2.3. Stability of TV and EV within the spherical aggregates

The percentage retention of TV and EV was calculated by the formula: [(vanillin at X storage time) × 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

To reconfirm the role of amylose on the half-life of TV and EV from the spherical aggregates, amylose was added from 10 to 40% to amaranth starch at incremental levels of 10%. The results are shown in Table 1. It is evident that all the spherical aggregates showed a decrease in EV and TV during the 6-week storage. Further, it can be seen that both

Table 2

Regression analysis and half-life ($t_{1/2}$) of TV and EV in the spherical aggregates (values within parenthesis indicate the correlation coefficient; using 1.0% gum Arabic as bonding agent; vanillin at 5%, bos) with time, of the amaranth starch/amylose blend

Amylose content (%)	Regression analysis and half-life ($t_{1/2}$) (weeks)			
	TV		EV	
	Regression equation	$t_{1/2}$	Regression equation	$t_{1/2}$
0	$Y = -0.0189x + 4.61$ ($R^2 = 0.98$)	36.67	$Y = -0.0219x + 4.6045$ ($R^2 = 0.99$)	31.64
10	$Y = -0.0189x + 4.5961$ ($R^2 = 0.94$)	36.67	$Y = -0.025x + 4.5996$ ($R^2 = 0.96$)	27.72
20	$Y = -0.0183x + 4.5945$ ($R^2 = 0.90$)	37.87	$Y = -0.0259x + 4.6008$ ($R^2 = 0.99$)	26.76
30	$Y = -0.0232x + 4.5996$ ($R^2 = 0.92$)	29.87	$Y = -0.0306x + 4.5954$ ($R^2 = 0.97$)	22.65
40	$Y = -0.0499x + 4.5766$ ($R^2 = 0.92$)	13.89	$Y = -0.1085x + 4.6056$ ($R^2 = 0.98$)	6.39

TV and EV decreased when amylose was added to amaranth starch. For instance, EV in the spherical aggregates prepared from amaranth starch was 83.0%. This decreased to 66.6% at 10% addition of amylose, to 63.4% at 20% amylose, 58.2% at 30% amylose and finally 54.2% at 40% addition of amylose. This trend continued throughout the six-week storage period. While the EV decreased from 83.0 to 73.0% in case of spherical aggregates from amaranth starch alone during a six-week storage, the corresponding values for vanillin with spherical aggregates prepared from 40% amylose blend to amaranth starch ranged from 54.5 to 27.8%. A similar pattern was visible in case of TV.

A semi-log plot of ln (% retention of EV) and ln (% retention of TV) vs. storage time (Figs. 1 and 2) showed linear pattern indicating a first order degradation kinetics. Table 2 compares the regression analysis and the half-life of the TV and EV in the spherical aggregates prepared from amaranth starch/mylose blends. It is very clear from this table that introduction of incremental levels of amylose decreases the half-life of both TV and EV progressively. From the results obtained in this work, it may be hypothesized that the aggregates prepared from amaranth starch containing added amylose is porous in nature; the porosity increasing with increasing amounts of added amylose.

All these observations reconfirm the previously observed role of amylose on the stability of vanillin entrapped within the spherical aggregates. It would be interesting to see the if this also holds true for the modified starches, and for chemically distinct components with the native starches.

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