Emulsification and Microencapsulation Properties of Gum Arabic

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Emulsions of gum arabic solutions (10% w/w) and soya oil at oil/gum ratios of 0.25−5.0 were prepared by homogenization at 20 MPa. The resulting emulsions were subsequently spray-dried to produce powders with oil contents ranging from 20 to 82% (w/w). Lipid globule size distributions and viscosities of the emulsions were determined, and particle size and percentage of extractable oil were determined for the spray-dried powders. The ability of the powders to redisperse in water was also examined. The average lipid globule size ($D_{4,3}$) (0.57 μm) did not vary significantly ($P > 0.05$) as the oil/gum ratio was increased from 0.25 and 1.0, but it did increase at higher ratios to a maximum of 2.02 μm. The average particle size of the spray-dried emulsions was within the range 9−17 μm, and the microencapsulation efficiency decreased from 100 to 48% when the oil/gum ratio was increased from 0.25 to 5.0, respectively. Powders with an oil content <50% dispersed readily in water.

Keywords: *Gum arabic; emulsions; microencapsulation; lipid globule size distribution*

INTRODUCTION

Microencapsulation may be defined as the packaging or coating of liquids, solids, or gases with a thin protective layer or wall material, which inhibits volatilization and protects against chemical deterioration. Spray-drying emulsions is a particularly effective means of microencapsulating chemically reactive oils, volatile oils, and flavor compounds. Spray-dried powder particles contain the encapsulated material as minute droplets embedded within its wall. Microencapsulation has also become an attractive approach for transforming liquid food flavorings into stable free-flowing powders that are easy to handle and incorporate into a dry food mix. Gum arabic (gum *Acacia*) is a hydrocolloid produced by the natural excudation of acacia trees and is an effective encapsulation agent due to its high water solubility, the low viscosity of concentrated solutions relative to other hydrocolloid gums, and its ability to act as an oil-in-water emulsifier (Glicksman, 1983).

Gum arabic is composed of a highly branched arrangement of the simple sugars galactose, arabinose, rhamnose, and glucuronic acids (Anderson and Stoddart, 1966; Street and Anderson, 1983) and also contains a protein component (∼2% w/w) covalently bound within its molecular arrangement (Anderson et al., 1985). The protein fraction plays a crucial role in determining the functional properties of gum arabic (Randall et al., 1988). Gum arabic is produced in areas that are subject to unpredictable climatic variations and political turbulence, which can interrupt supply of the product. Therefore, there has been considerable incentive in recent years to find total or partial replacers for gum arabic. Maltodextrins and chemically modified starches have been investigated as replacers for gum arabic in spray-dried emulsions (Amandaraman and Reineccius, 1987; Bangs and Reineccius, 1988; Kenyon and Anderson, 1988; Trubiano and Lacourse, 1988). To wholly or partially replace gum arabic as an encapsulating agent, it is essential to understand its emulsifying properties. Whereas many of the properties of gum arabic stabilized emulsions have been extensively studied (Anker and Reineccius, 1988; Thevenet, 1988; 1995; Dickinson et al., 1989; Ray et al., 1995; Kim et al., 1996), the effect of the ratio of oil/gum arabic has not been systematically investigated. This forms the basis of the work reported here.

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EXPERIMENTAL PROCEDURES

Materials. Gum arabic obtained from Sigma Chemical Co. (Poole, Dorset, England) and refined soya oil obtained from Anglia Oils Ltd. (Kingston-upon-Hull, North Humberside, England) were used to prepare the emulsions. Analysis of the gum arabic confirmed it to be *Acacia senegal* (Anderson et al., 1985, 1991). The moisture content, determined by drying, was 10.9%, the percentage nitrogen, determined by macro-Kjeldahl, was 0.33%, and the specific rotation was −31°. All other reagents used in the analysis were of GPR grade and were obtained from BDH Laboratories Ltd. (Poole, Dorset, England).

Emulsion Preparation. An aqueous solution of gum arabic (10% w/v) was prepared and stirred overnight at 20−25 °C. Although it is recognized that many workers have reported the benefits from using higher total solids concentrations (Reineccius and Bangs, 1985), a 10% concentration was employed to facilitate the investigation of high oil/gum ratios. Emulsions with oil/gum ratios of 0.25, 0.5, 0.75, 1.0, 2.0, 3.0, 4.0, or 5.0 were prepared by adding the gum arabic solution to a preweighed quantity of soya oil. Pre-emulsions were prepared by blending the gum solution/oil mixtures for 1 min at 6500 rpm using a laboratory mixer (Silverson L4RT, Silverson Machines Ltd., Chesham, Bucks., England) fitted with an emulsifier screen. The pre-emulsions were then further homogenized at 20 MPa with five recirculations using a piston homogenizer (Niro Soavi, Parma, Italy).

Spray-Drying the Emulsion. The emulsions were spray-dried using a laboratory spray-drier (LabPlant SD-04, Huddersfield, West Yorkshire, England) fitted with a 0.5 mm jet nozzle atomizer. The product was fed to the spray-drier at room temperature at a rate of 30 mL/min, and the inlet and

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outlet temperatures were maintained at 180 and 100−120 °C, respectively. The dried powders were collected and subsequently stored in opaque containers at 4 °C.

Particle Size Analysis. The particle size distributions of the emulsion lipid droplets and the spray-dried microcapsules were determined using a Malvern Mastersizer S fitted with a small volume sample presentation unit and integration software (Malvern Instruments Ltd., Worcs., England). Calculation of the particle size distributions was based on a relative (to that of the surrounding medium) particle refractive index of 1.1500 and a particle absorption of 1.0000. Distilled water was used as the dispersant for the determination of the emulsion lipid globule size distribution. Powder particle size distributions were determined following their dispersion in propan-2-ol.

Emulsion Viscosity. Viscosity measurements were made using a controlled stress rheometer (Physica-Rheolab MC100, Paar Scientific Ltd., Raynes Park, London, England) fitted with a double concentric cylinder measuring geometry (MS-Z1 DIN). The viscosity was measured at a shear rate of 50 s^{-1} over a time period of 1200 s at 25 °C, and the apparent viscosity was taken as the average value recorded over this time.

Determination of Total and Free Oil of Spray-Dried Powders. The total oil content of the powders was determined by the Mojonnier modification of the Röse Gottlieb test as prescribed for milk powders (Richardson, 1988). Free oil on the powders was extracted by gently mixing a powder sample (2.5 g) in petroleum ether (100 mL) for 15 min at 25 °C in a 250 mL sealed glass bottle. The solvent was filtered (Whatman No. 41), an aliquot of the filtrate (50 mL) was evaporated to dryness in a preweighed round-bottom flask using a rotary evaporator, and the extractable fat was determined gravimetrically. Microencapsulation efficiency (ME) was calculated as follows:

$$ME = [(\text{total oil} - \text{free oil})/\text{total oil}] \times 100$$

Scanning Electron Microscopy (SEM). Powder specimens were adhered to sample stubs using double-sided tape. The specimens were sputter coated with gold using a Polaron sputter coater E5100 (VG Microtech, East Sussex, England, U.K.) and examined using a JEOL JSM-5419 LV scanning electron microscope (JEOL U.K. Ltd., Welwyn Garden City, Herts., England, U.K.) at an accelerating voltage of 15 kV.

Redispersibility of Powders in Water. The ability of the powders to redisperse in water was measured by mixing 0.5 g of powder with 150 mL of water (using a magnetic stirrer) at 20−25 °C for 30 min. The particle size distribution of the resultant dispersion was determined using the Mastersizer as previously described.

Statistical Analysis. All results represent the means of four replicates. Statistical analyses were performed using the SAS package. Statistical significance was determined by analysis of variance (ANOVA). P values of <0.05 were deemed statistically significant.

RESULTS AND DISCUSSION

Particle Size and Viscosity. The lipid globule size distributions of the gum arabic stabilized emulsions at the oil/gum ratios examined are shown in Figure 1, and the calculated volume average lipid globule sizes ($D_{4,3}$) for the emulsions are shown in Table 1. The size distribution curves were unimodal and showed a normal distribution. There was no significant variation in the $D_{4,3}$ ($P > 0.05$) values of the emulsions (0.57 μm) when the oil/gum ratio was increased from 0.25 to 1.0. However, as the oil content of the emulsions was increased further, $D_{4,3}$ increased linearly ($R^2 = 0.995$) up to a maximum of 2.02 μm. These results suggest that at oil/gum ratios between 1.0 and 2.0, the quantity of gum arabic available to act as an emulsifier becomes limiting, resulting in the production of larger oil droplets and thus reducing the specific fat surface area requiring stabilization. The $D_{4,3}$ values of the emulsions prepared with oil/gum ratios <2.0 were <1 μm, which is the diameter quoted by Thevenet (1988) as being sufficient to produce stable gum arabic emulsions.

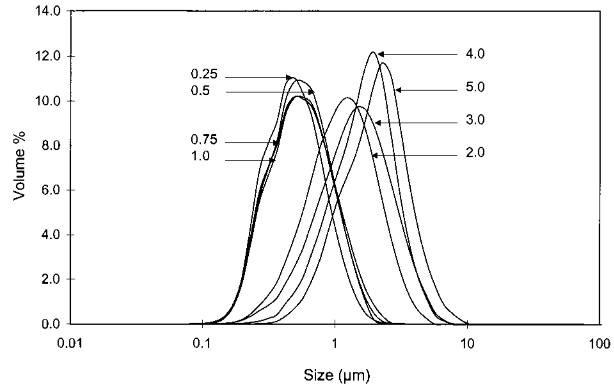

Figure 1. Effect of soya oil/gum arabic ratios 0.25, 0.5, 0.75, 1.0, 2.0, 3.0, 4.0, and 5.0 on the lipid globule size distributions of gum arabic stabilized emulsions.

Table 1. Oil Content and Particle Size Characteristics of Gum Arabic Stabilized Emulsions and Spray-Dried Emulsions as a Function of Oil/Gum Ratio

oil/gum ratio	total oil content (wt % total solids)	av emulsion lipid particle size ($D_{4,3}$) (μm)	av powder particle size ($D_{4,3}$) (μm)
0.25	20.4	0.58	10.6
0.50	33.0	0.52	11.2
0.75	43.4	0.58	9.4
1.00	50.2	0.60	11.3
2.00	67.8	1.03	10.3
3.00	74.4	1.55	12.8
4.00	79.4	1.75	15.8
5.00	82.0	2.02	17.3

The average powder particle sizes for the spray-dried emulsions showed no significant variation ($P > 0.05$) as the oil/gum ratio was increased from 0.25 to 2.0. However, the $D_{4,3}$ of the powders prepared at oil/gum ratios of 4.0 and 5.0 increased significantly to 15.8 and 17.3 μm, respectively (Table 1). The droplet size of an atomized emulsion and, hence, powder particle size are influenced by the nozzle port size, position of the spray nozzle, liquid delivery rate, atomizing air pressure, and solution concentration (viscosity) (Jones, 1988). In this study, all of the emulsions were spray-dried under identical conditions; consequently, the observed variations in particle size are most likely due to changes in total solids concentration or viscosity. As illustrated in Figure 2, the emulsion viscosity increased in a logarithmic fashion as the oil content was increased, so it is plausible that as the oil/gum ratio of the emulsion was increased the apparent viscosity increased, resulting in less efficient atomization. In addition, the large differences in powder particle size may be attributed to the extensive clumping of high-oil powders (Figure 3) coupled with the extensive shrinkage and contraction of the low-oil powders (Figure 4).

Determination of Total and Free Oil. The results from the total oil determination of the powders reflect 100% recovery of the fat, based on the composition of the original emulsion. One exception was the emulsion prepared at the oil/gum ratio of 5.0, for which the measured oil content was 1−2% lower than expected, which may indicate some free oil loss during the manufacture of the powder.

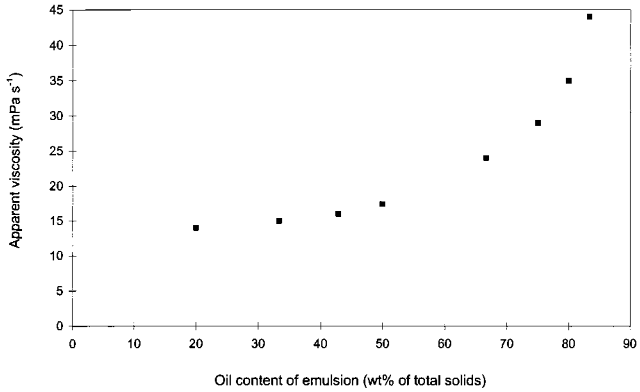

Figure 2. Effect of increasing oil content on the apparent viscosity of gum arabic stabilized emulsions.

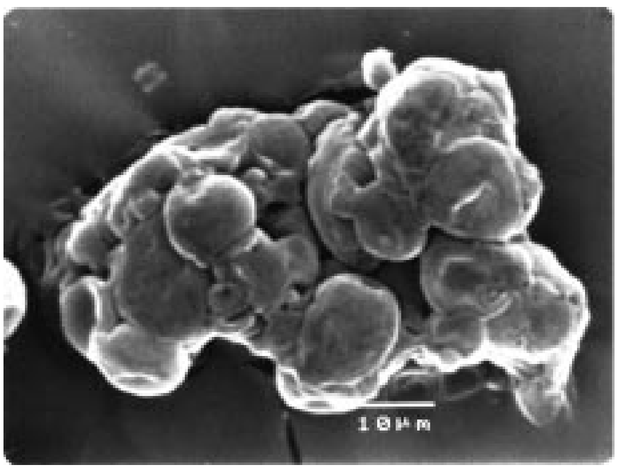

Figure 3. Scanning electron micrograph of a fresh spray-dried emulsion prepared at an oil/gum ratio of 5.0 (×2000). (Figure is reproduced here at 50% of its original size.)

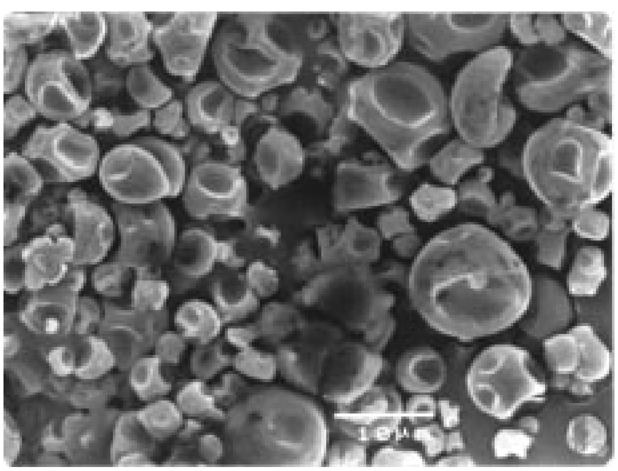

Figure 4. Scanning electron micrograph of a fresh spray-dried emulsion prepared at an oil/gum ratio of 0.25 (×2000). (Figure is reproduced here at 50% of its original size.)

Figure 5 illustrates the microencapsulation efficiencies (ME) of the spray-dried powders. The treatment of the powders involved in the determination of ME is designed to remove only surface oil and oil exposed to the atmosphere through cracks in the surface of the powder particle. It would appear, however, that as the treatment is applied to powders of increasing oil content, the degree of oil extraction increases so much that the resultant ME would represent more than simply surface or subsurface oil. This is supported by the SEM micrographs of freshly prepared powders (Figure 3) and solvent-extracted powder of oil/gum ratio 5.0 (Figure 6). The high-oil powder was visible as clumps of particles that seem to have fused together. It is possible that this would result from the presence of large quantities of surface oil on the powders (Figure 3). When these powders were treated with an organic solvent, the particles were seen to exist as more discrete spherical units and incomplete shells of microcapsules (Figure 6). It seems that when the oil is removed from these particles, the structure is weakened and the thin gum arabic matrix that remains becomes disrupted.

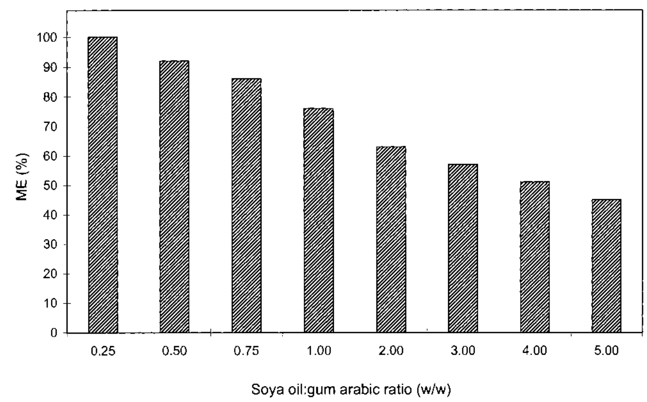

Figure 5. Effect of oil/gum ratio on the ME of spray-dried gum arabic stabilized emulsions.

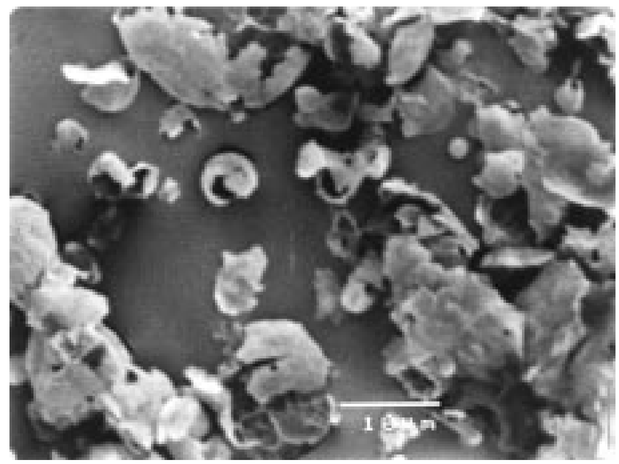

Figure 6. Scanning electron micrograph of a solvent extracted spray-dried emulsion prepared at an oil/gum ratio of 5.0 (×2000). (Figure is reproduced here at 50% of its original size.)

ME ranged from a maximum of 100%, in the case of powders prepared at an oil/gum ratio of 0.25, to 42% for the powders prepared at the oil/gum ratio of 5.0 (Figure 5). In the powders at the higher oil/gum ratios (2.0−5.0), the larger lipid particles would have provided larger quantities of surface oil for extraction resulting in a low ME. This is consistent with the findings of Brenner (1983) and Trubiano and Lacourse (1988). However, it would appear that at the lower oil/gum ratios (<1.0), ME was influenced to a greater degree by the decreasing quantity of gum arabic available to provide the structural matrix that holds the encapsulated lipid particles together.

Other workers have examined the influence of increasing oil/gum ratio on the ME of gum arabic stabilized spray-dried emulsions (King et al., 1976). They also report a decrease in ME (from 99.9 to 29.0%) when oil/gum ratio was increased from 0.25 to 1.0. However,

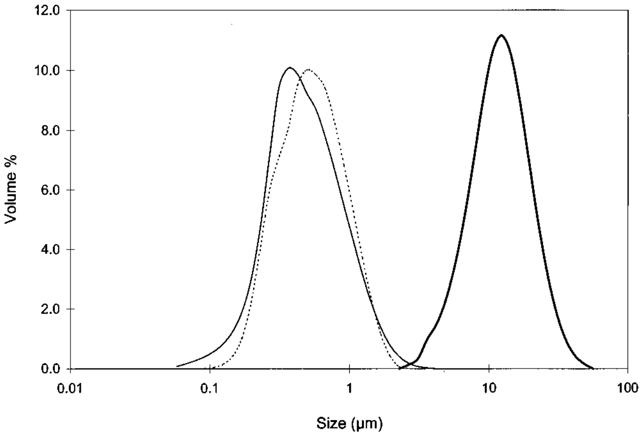

Figure 7. Particle size distribution of a gum arabic stabilized emulsion (solid line), a spray-dried emulsion (heavy solid line), and a redispersed spray-dried emulsion (dashed line) prepared at an oil/gum ratio of 0.25 (20% oil dry wt).

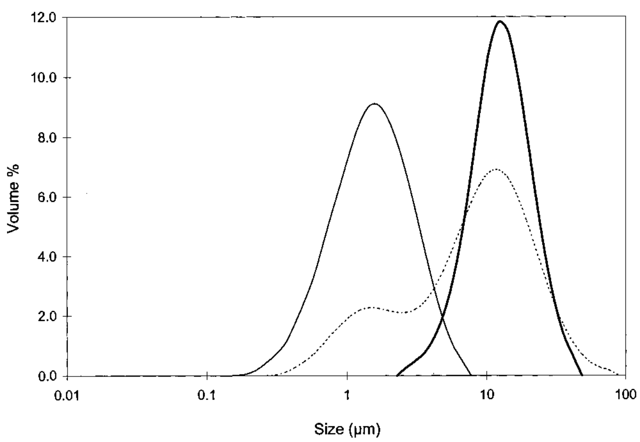

Figure 8. Particle size distribution of a gum arabic stabilized emulsion (solid line),a spray-dried emulsion (heavy solid line), and a redispersed spray-dried emulsion (dashed line) prepared at an oil/gum ratio of 3.0 (75% oil dry wt).

comparison of these ME values with those reported by other workers is difficult due to the variety of methods used for determining ME. It would be expected that the encapsulation efficiencies for spray-dried, gum arabic stabilized emulsion published by King et al. (1976) should be lower than those determined in this study as their solvent extraction method involved the use of the more thorough Soxhlet extraction, coupled with the fact that the oil which they encapsulated was the low-viscosity and volatile orange flavor oil.

Redispersibility of the Powders. Figures 7 and 8 represent the lipid particle size distributions of the emulsions, the powder particle size of the dried emulsions, and the lipid particle size of the redispersed dried emulsions containing 20 and 75% oil, respectively. The lipid particle size distributions for the original emulsion and the redispersed dried emulsion are very similar for the powder prepared from the emulsion with an oil/gum ratio of 0.25 (Figure 7) with only small differences in their $D_{4,3}$ (0.58 μm for the emulsion, 0.67 μm for the redispersed dried emulsion). This represents the desired attributes of a spray-dried powder: a rapid redispersion in water with little evidence of lipid droplet coalescence or aggregation and complete dissolution of the encapsulation material. The particle size characteristics of the emulsion and dried emulsion and redispersed dried emulsions prepared at an oil/gum ratio of 3.0 (75% oil) are shown in Figure 8. The size distribution curve of the redispersed dried emulsion showed a bimodal distribution indicating incomplete dissolution. The peak with a mode of 10−15 μm possibly represents undissolved powder particles, whereas the peak with a mode of 1−2 μm represents emulsified lipid droplets. Increasing the redispersion time from 0.5 to 24 h did not improve the redispersion properties of this dried emulsion (data not shown). The poor redispersion characteristics of this powder and other high-oil powders may be due to their high free oil content, as indicated by ME values of <57%. The average powder particle size of the spray-dried emulsions of oil/gum ratios 0.25 and 3.0 showed only slight variation ($D_{4,3}$ = 10.6 and 12.8 μm, respectively).

Much of the literature on the assessment of spray-dried emulsions places primary importance on surface oil measurements, the results of which are an important indicator of the degree of volatilization or degradation of encapsulated oils. However, the ability of the spray-dried emulsion to reconstitute in water should also be viewed as an equally important property of a microencapsulation system as in most cases it is necessary that the product should be encapsulated in a way which facilitates its subsequent dispersion.

ABBREVIATIONS USED

$D_{4,3}$, volume average diameter (lipid globule size); ME, microencapsulation efficiency; SEM, scanning electron microscopy.

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