The Effects of Rheological Properties of Wall Materials on Morphology and Particle Size Distribution of Microcapsule

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Abstract

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The effects of rheological properties of the wall materials on the morphology and particle size distribution of microcapsules prepared by spray-drying were evaluated. Gelatin-sucrose (Gel-Suc), gelatin-peach-gum-sucrose (Gel-PG-Suc), and HI-CAP 100 were used as wall materials with vitamin A as a model core material. Scanning electron microscopy (SEM) showed that microcapsules produced with Gel-Suc exhibited cracks while Gel-PG-Suc produced a smooth surface with few pores, and HI-CAP100 a rounded surface containing characteristic concavities. The volume average diameter ($D_{4,3}$) showed significant variations from 73.9 ± 1.02 μm and 68.7 ± 0.85 μm to 29.9 ± 0.94 μm ($P < 0.05$). Rheometry indicated that the wall paste viscosity was inversely proportional to the shear rate. Viscosity ranking was Gel-Suc > Gel-PG-Suc > HI-CAP 100. Gel-Suc showed the highest elastic modulus (G') and viscous modulus (G'' values), followed by Gel-PG-Suc and HI-CAP 100. Gel-Suc was associated with moderate quantities of broken microcapsules while HI-CAP 100 generated numerous microcapsules with characteristic dents generated during spray-drying.

Keywords: microcapsule; wall materials; rheological properties; morphology; particle size; spray-drying

Microencapsulation is a technology to entrap sensitive ingredients or core materials in a protective polymer or wall material. It protects the core materials from adverse environmental conditions, thus enhancing their stability and range of applications (Hogan *et al.* 2001). Spray-drying is one of many standard methods to microencapsulate food ingredients. Microencapsulation has become an attractive approach to transform liquid foodstuffs into stable and free-flowing powders for more convenient incorporation into dry food systems (Teixeira *et al*. 2004). It also often involves a variety of biopolymers derived from natural gums, proteins, modified starches, and their blends (Sheu & Rosenberg 1998; Adhikari *et al.* 2003; Muthukumarasamy *et al*. 2006). These biopolymers serve as wall materials with desirable properties such as a good solubility, but they differ in interfacial functionality and rheological properties (Fortuna *et al*. 2004; Weinbreck & Wientjes 2004; Norziah *et al*. 2006). Their flexibility or rigidity also play an important role in their structure-function relationship and in commercial applications in the food and biomedical industries (Morrisa *et al*. 2008). Most notably, Pedroza-Islas *et al*. (1999) reported that particle size and microcapsule microstructure varied with the biopolymers selected as wall materials.

This study aimed at (1) comparing the morphology and particle size distribution in microcapsules produced with microencapsulants based on Gel-Suc, Gel-PG-Suc, and HI-CAP 100; (2) investigat-

ing the rheological properties of wall material pastes; and (3) analysing the effects of rheological properties of wall materials on the morphology and particle size distribution of vitamin A microcapsules.

MATERIALS AND METHODS

Materials. Type B porcine gelatin (bloom strength 200) was purchased from Hangzhou Qunli Gelatin Chemical Co., Ltd. (Hangzhou, China). Peach gum was purchased from Shandong Ruenyuan Industry Co., Ltd. (Rizhao, China). HI-CAP 100 (starch octenylsuccinate) was donated by National Starch & Chemical (Shanghai,China). Vitamin A acetate came from Beijing Long Age Vita Nutrition Products Co., Ltd. (Beijing, China). Sucrose was of food grade; diethyl ether and isopropyl alcohol were of analytical grade.

Preparation of microcapsules by spray-drying. The microcapsules were prepared by oil-in-water (O/W) emulsification and spray-drying (Soottitantawat *et al*. 2004). The wall material solution was dissolved in warm distilled water (70°C) under constant stirring at 400 rpm for 10 min, then covered and left overnight at room temperature. The core material was a 30% (w/w) solution of vitamin A acetate dissolved in coconut oil. The optimum matrix parameters for the core-to-wall ratio and total solids concentration were 1:3 (w/w) and 30% (w/v) for Gel-Suc-based solution and Gel-PG-Suc solution as compared to 1:1.5 (w/w) and 40% (w/v) for HI-CAP 100-based solution. The core material was added into the wall material solution under agitation and then dispersed at high speed (10 000 rpm, 1 min). The mixtures were homogenised at 33 MPa and then at 27 MPa at room temperature (Homogenizers JHG-Q54-P60, Soontrue Enterprise Co., Ltd., Foshan, China). The emulsions were spray-dried at a feed rate of 1000 ml/min (QZ-5 high-speed centrifugal spray drying machines, Wuxi city Dongsheng Drying Equipment Plant, China). The air inlet and air outlet temperatures were 180°C and 80°C, respectively.

Microencapsulation efficiency. The total and external vitamin A contents of the microcapsules were determined according to AACC standards (AACC 2000). External vitamin A was determined by vigorously shaking the microcapsules (0.10 g) in diethyl ether (25 ml) in a 150 ml conical flask at 25°C for 10 minutes. The solvent was filtered and transferred to a saponification flask. Total vitamin A content was determined by vigorously shaking the microcapsules (0.05 g) in distilled water (25 ml, 70~80°C) for 30 min followed by the transferr to a saponification flask. When saponification and separation were completed, the samples were loaded into matched cells in isopropyl alcohol and then placed in spectrophotometer (UV-2800, UNICO Co. Ltd, Shanghai, China). The absorbance of the test solutions was determined at 310 nm, 325 nm, and 334 nm. Vitamin A content and microencapsulation efficiency (ME) were calculated according to the previous report (McNamee *et al*. 1998).

$$ME = [(\text{total vitamin A} - \text{external vitamin A})/\text{total vitamin A}] \times 100 \ (\%)$$

Scanning electron microscopy of microcapsules. Microcapsule specimens were fixed in 2.5% glutaraldehyde for 1 h at 4°C, rinsed in 0.1M phosphate buffer several times, and post-fixed in 1% osmium tetroxide for 30 min at 4°C. After several rinses in 0.1M phosphate buffer, the specimens were dehydrated in a graded ethanol series before the critical point of drying (CPD-030, BAL-TEC Co., Reading, UK). The dried samples were affixed to an aluminum stub with double-stick tape, coated with gold in an ionic sputter coater (SCD-005, BAL-TEC Co., Reading, UK). They were viewed and photographed by SEM (QUANTA-200, FEI Co., Eindhoven, the Netherlands). SEM settings were: objective aperture, 100 μm and accelerating voltage, 10 kV. Direct examinations were made at 600 × power (Pedroza-Islas *et al*. 1999).

Particle size distribution of microcapsules. The particle size distribution was obtained on Mastersizer 2000 particle size analyser (Malvern Instruments, Malvern, UK). The particle size distribution and average particle size were analysed in quadruplicates. The solution was sonicated for 1 min using anhydrous ethanol as dispersant, and the analyses for the particle size distribution were performed under constant stirring (Pedroza-Islas *et al*. 1999).

Viscosity measurement of wall material pastes. The viscosity of Gel-Suc and Gel-PG-Suc-based pastes at 30% (w/w) as well as HI-CAP-100-based paste at 40% was determined by a stable procedure using an AR 1000 rheometer (TA Instruments, Ltd., Crawley, UK) equipped with parallel-plate geometry of 40 mm diameter and 1 mm gap geom-

etry. The specimens were set on the central ram of the rheometer and covered with silicon oil to prevent water evaporation during the measurement. For the viscosity measurement, the shear rate was scanned from 0 1/s to 100 1/s at 80°C (Tan *et al*. 2007a).

Rheological measurement of wall materials pastes. The rheological behaviour of Gel-Suc- and Gel-PG-Suc-based pastes at 30% (w/w) as well as of HI-CAP 100-based paste at 40% was determined by the dynamic procedure using an AR 1000 rheometer (TA Instruments, Ltd., Crawley, UK) equipped with parallel-plate geometry of 40 mm diameter and 1 mm gap geometry. As above, the specimens were set on the central ram of the rheometer and covered with silicon oil to prevent water evaporation during the measurement. The scans were performed in triplicates; both elastic modulus (G') and the viscous modulus (G'') were recorded. Oscillatory stress was scanned from 1~1000 Pa at 5 rad/s and 80°C (Tan *et al*. 2007a).

Statistical analysis. The results of the particle size distribution of the microcapsules reflected the mean of four replicates in each case. Statistical analyses were performed using Statistic Analysis System 8.2 (SAS, 1999). The statistical significance was determined by analysis of variance (ANOVA). The differences were considered to be statistically significant at $P < 0.05$.

RESULTS AND DISCUSSION

Optimum microencapsulation efficiency (ME) for all wall matrices is shown in Table 1. The ME values reflected the presence of oil on powder particle surfaces and the degree to which the matrices inhibited the extraction of internal oil by leaching. The core/wall ratio, total solids concentration, and wall material exerted a significant influence on ME ($P < 0.05$). The decrease in ME may have resulted from the wall material being insufficient to produce a sufficiently strong structural matrix, and from insufficiently thick layers of the wall material between the encapsulated oil droplets (Hogan *et al.* 2001). ME improved with increasing total solids concentration, which confirms the findings of the colleagues (Sheu & Rosenberg 1998). However, an increase of total solids concentration in the wall materials led to a higher viscosity of the emulsion, causing spray-drying to fail.

The microcapsules from all three wall materials were spherical and non-agglomerating (Figure 1), which indicated satisfactory flow properties. SEM micrographs showed that the blend of wall material biopolymers influences the outer topography or morphology of microcapsules (Pedroza-Islas *et al*. 1999). More specifically, some microcapsules produced with Gel-Suc exhibited cracks, pores, and breakage (Figure 1A), creating a risk of the premature release of the core material (Rosenberg *et al.* 1985). The microcapsules obtained with Gel-PG-Suc presented a smooth surface with few pores and without cracks (Figure 1B) (Xie *et al*. 2006). The microcapsules encapsulated with HI-CAP 100 presented rounded external surfaces with characteristic concavities while the outer surfaces showed no visible holes or fractures, which is a reliable indicator of the efficiencies of the preparation before spray drying and of microencapsulation (Figure 1C). Almost all microcapsules produced with HI-CAP 100 presented surface dents, which was attributed to the mechanical atomisation, drying, and cooling solidification involved in spray-drying (Rosenberg *et al*. 1985). During spray-drying, rapid cooling generated dents due to the wall material shrinkage, especially at high drying rates (Sheu & Rosenberg 1998; Teixeira *et al*. 2004). Sheu and Rosenberg (1998) reported that whey proteins improved the surface smoothness and decreased the surface indentation of maltodextrin-based microcapsules. Combinations of whey protein isolates (WPI) with high-DE carbohydrates limited the surface dent formation better than those with low-DE carbohydrates. More broadly, dents have also been related with

Table 1. Effect of wall materials on microencapsulation efficiency at optimum matrix

Wall materials	Wall materials ratio (w/w)	Core/wall ratio (w/w)	Total solids concentration (w/v %)	Microencapsulation efficiency (%)
Gel-Suc	1:6	1:3	30	94.77 ± 0.74
Gel-PG-Suc	1:1:8	1:3	30	96.70 ± 0.86
HI-CAP 100	1	1:1.5	40	97.85 ± 0.61

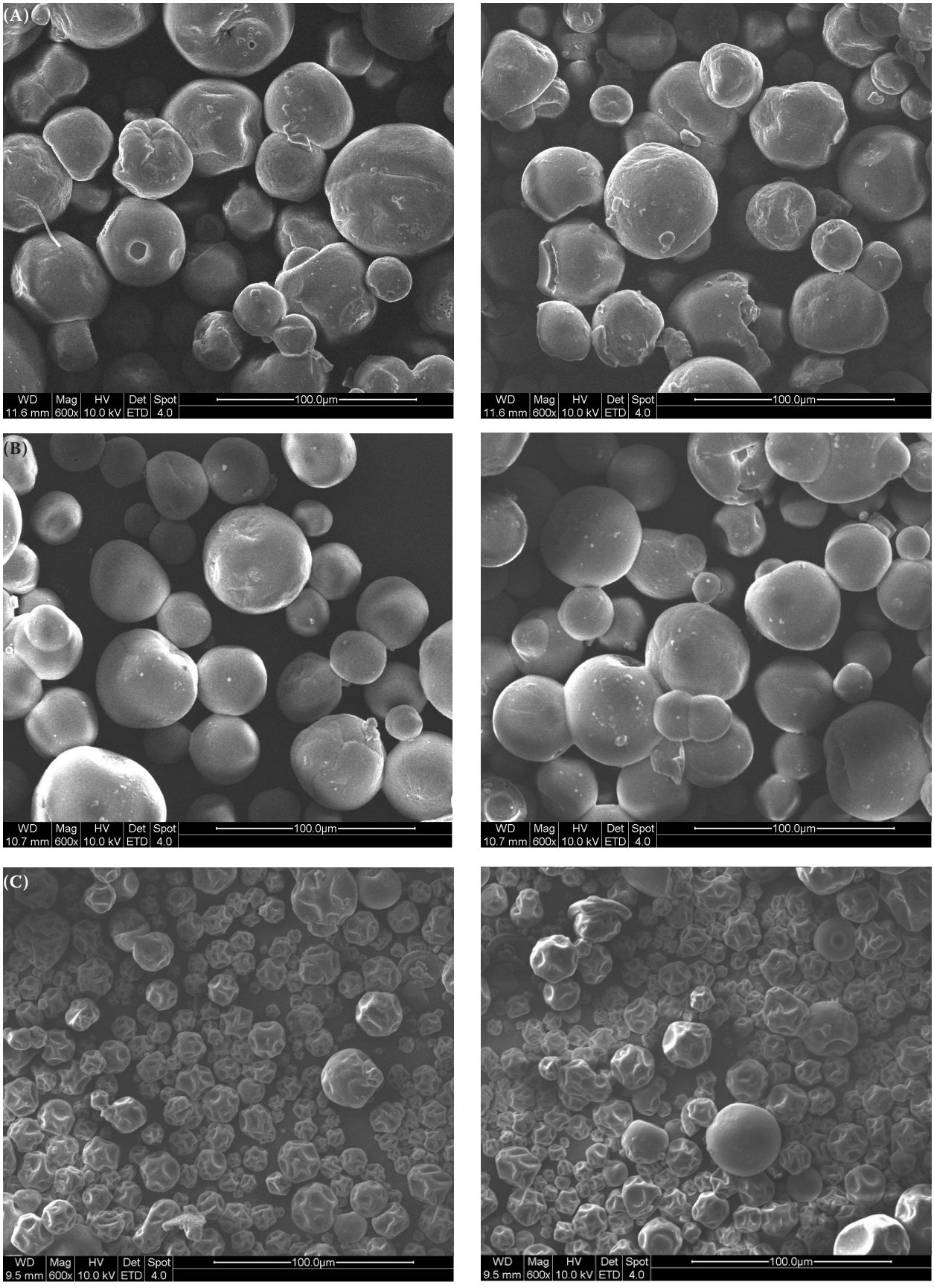

Figure 1. SEM micrographs of microcapsules: A – Gel-Suc-based, B – Gel-PG-Suc-based, C – Hi-CAP-based

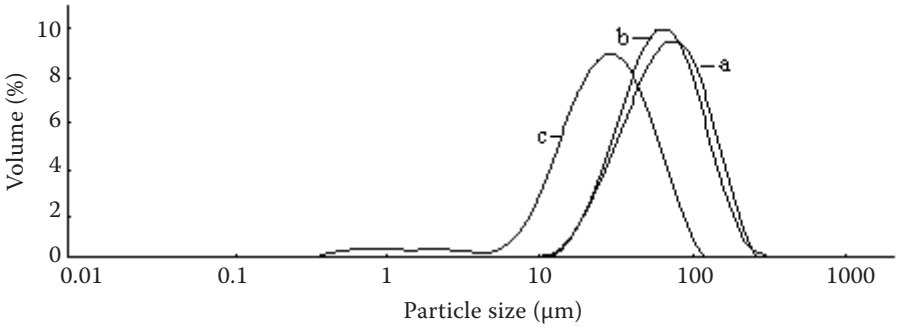

Figure 2. Particle size distribution of microcapsules: a – Gel-Suc-based, b – Gel-PG-Suc-based, c – Hi-CAP-based

the wall materials containing high proportions of carbohydrates (Pedroza-Islas *et al.* 1999).

The size distribution showed normal, unimodal distribution (Figure 2). The distribution of Gel-Suc-based microcapsules was observed to peak in the range from 69.2 μm to 79.4 μm, d(0.1) ≤ 27.4 μm, d(0.5) ≤ 64.2 μm ≤ d(0.9) ≤ 133.8 μm, with a volume average diameter ($D_{4,3}$) = 73.9 μm. The peak of Gel-PG-Suc-based microcapsules was observed in the range from 60.3 μm to 69.2 μm, d(0.1) ≤ 27.2 μm ≤ d(0.5) ≤ 59.0 μm ≤ d(0.9) ≤ 122.5 μm, $D_{4,3}$ = 68.7 μm. Finally, the peak of HI-CAP 100-based microcapsules was in the range from 26.3 μm to 30.2 μm, d(0.1) ≤ 9.8 μm ≤ d(0.5) ≤ 25.7 μm ≤ d(0.9) ≤ 56.8 μm, $D_{4,3}$ = 29.9 μm. $D_{4,3}$ varied significantly between different wall material matrices ($P < 0.05$). The particle droplet size was influenced by spray nozzle size, nozzle position, liquid delivery rate, atomising pressure, and solution concentration (viscosity) (McNamee *et al.* 1998). All emulsions in this study were spray-dried under identical conditions and therefore any variations in the particle size were most likely due to the differences in viscosity. Hogan *et al.* (2001) reported that the decrease of the sodium caseinate/DE 28 ratio from 1:4 to 1:49 caused a marginal increase in $D_{4,3}$. The differences between the particle size distribution affected the core material retention and other microcapsule properties (Hong *et al.* 2002).

Figure 3 illustrates the effect of shear rate on the viscosity of wall material pastes. The viscosity of the same mass fraction of paste for all three wall materials was inversely proportional to the shear rate while the viscosity ranking was Gel-Suc > Gel-PG-Suc > HI-CAP 100. All three pastes were categorised as non-Newtonian fluids with shear thinning specific to pseudoplastic fluids (Boger 1977). Viscosity reflects the molecular movement of a viscoelastic body, and different viscosities indicate differences in the molecular structure (Quintana *et al.* 2002). Where the molecular chains are long and heavily twisted, flow resistance is high and viscosity increases. Emulsions of lower viscosity atomise easily into small particles during spray-drying; higher viscosity emulsions do not. Therefore, particle size distribution is directly bound up with emulsion viscosity. This result finds support in particle size distribution (Figure 3) and elsewhere in the literature (Park *et al.* 2001).

The changes in G' of the wall material pastes were observed as stress increased gradually from 1 Pa to 1000 Pa (Figure 4A). The G' value of Gel-Suc was the highest, followed by Gel-PG-Suc and HI-CAP 100. G' value for HI-CAP 100 pastes fell sharply as stress rose yet it was not the lowest at the beginning of scanning. The rigidity of molecular chains contributed to the G' and reflected elasticity (Ahmed *et al.* 2008; Chung *et al.* 2008). A higher G' value for Gel-Suc indicates that rigid molecular chains are superior to flexible ones. For the hardness of Gel-Suc molecular structure, the moveable resistance of the molecular chain was strong. When external elastic deformation

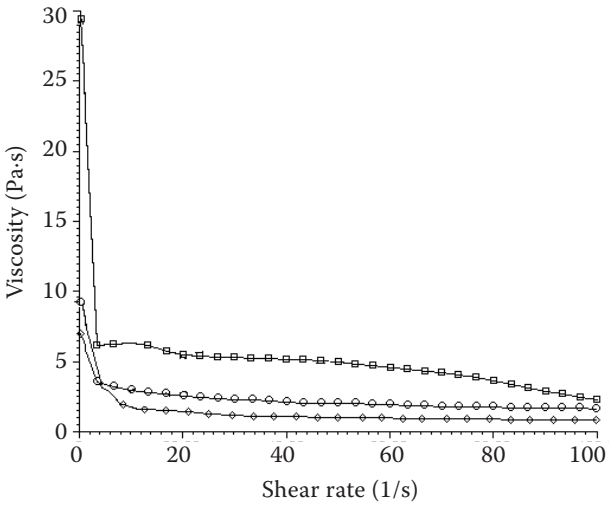

Figure 3. Viscosity vs shear rate of wall materials pastes: □ – Gel- Suc-based, ○ – Gel-PG-Suc-based, ◇ – Hi-CAP-based

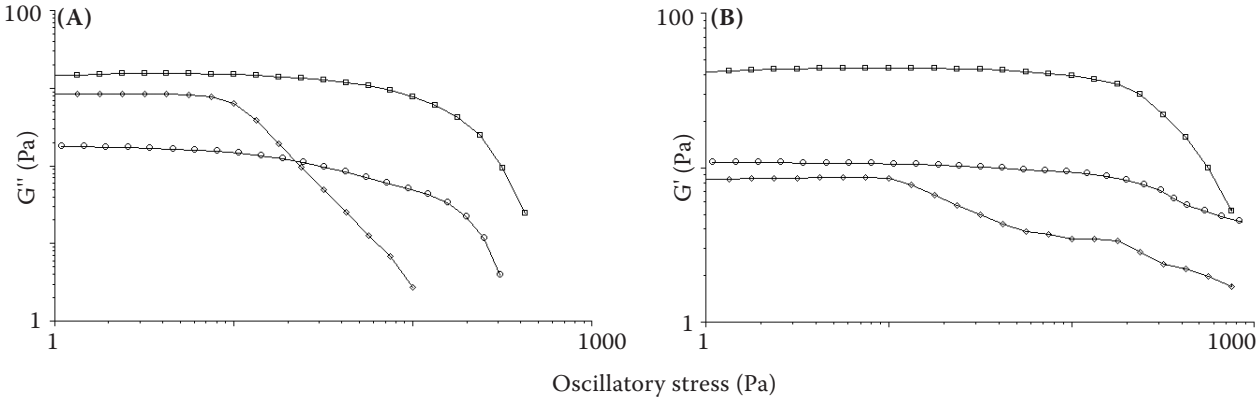

Figure 4. Elastic modulus and viscous modulus of wall materials pastes: □ – Gel-Suc-based, ○ – Gel-PG-Suc-based, ◇ – Hi-CAP-based

exceeded the stress endurance, stress fractures appeared (Özkan *et al*. 2002). From this we deduced that the rupturing of Gel-Suc-based microcapsules occurred during spray-drying. Unlike with Gel-Suc, G' for HI-CAP 100 was small, and the flexible molecular chain was superior. For the flexible chain, the molecular chain movement did not keep pace with the stress change and presented stress relaxation (Rosalina & Bhattacharya 2001). During the spray-drying, the hot air caused bulging in the membrane of HI-CAP 100 wall material. Microcapsule solidification was completed when the strain had not reverted because of the high rate of spray-drying. Therefore, the characteristic dents of microcapsules encapsulated with HI-CAP 100 were obtained.

The changes in paste G'' were observed with all three wall materials as stress increased gradually from 1 Pa to 1000 Pa (Figure 4B). G'' for Gel-Suc was the highest, followed by Gel-PG-Suc and HI-CAP 100. When stress acted on the wall material pastes and attempted at making them strain change, it needed to overcome the internal friction. The resistance in rigid molecular chains exceeded that in flexible molecular chains (Tan *et al*. 2007b). That flexible chains tended to orientate and arrange into patterns, but the rigid molecular chains did not, which was attributed to the highest G'' value of Gel-Suc value.

CONCLUSIONS

The volume average diameter ($D_{4,3}$) of microcapsules varied significantly: 73.9 ± 1.02 μm for Gel-Suc, 68.7 ± 0.85 μm for Gel-PG-Suc and 29.9 ± 0.94 μm for HI-CAP 100 ($P < 0.05$). Wall material viscosity ranking was Gel-Suc > Gel-PG-Suc > HI-CAP 100. The volume average diameter ($D_{4,3}$) of microcapsules showed a direct relationship to the wall material viscosity. Some microcapsules with Gel-Suc exhibited cracks, pores, and breakage during spray-drying. This was attributed to the highter elastic modulus (G') of Gel-Suc, which generated fragile fractures owing to the external elastic deformation force exceeding the stress endurance ability. The low G' of HI-CAP 100 suggested a poor recovery from deformation while the characteristic dents of microcapsules wrapped in HI-CAP 100 appeared when hot air induced bulging that failed to recover during the rapid solidification phase of spray-drying. This study therefore reports that the rheological properties of the wall materials affect both the morphology and particle size distribution of microcapsules.

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