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Encapsulation of sunflower oil in starch matrices via extrusion: effect of the interfacial properties and processing conditions on the formation of dispersed phase morphologies

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Abstract

In this study, the encapsulation of sunflower oil in a starch matrix via extrusion was investigated. The aim of this study was to get insight into the relations between the processing parameters, the hydrophile–lipophile balance (or the hydrophobic–hydrophilic balance; HLB) value of the emulsifier and the morphology of the dispersed phase. The obtained samples were analysed for their dispersed phase morphology using scanning electron microscopy. It was seen that the HLB value of the emulsifier affected the dispersed phase morphology. The average size of the dispersed oil droplets decreased with increasing HLB value, and was explained by the observed decrease in the interfacial surface tension between the starch melt and the oil phase. Average sizes of oil droplets also decreased with increasing screw speed, increasing melt temperature and decreasing throughput. The screw configurations also affected the average sizes of dispersed oil droplets. Especially dispersive mixing elements and kneading blocks favour the formation of smaller dispersed oil droplets. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Encapsulation in starch matrices; Extrusion; Hydrophile–lipophile balance (HLB); Processing conditions

1. Introduction

Encapsulation techniques for the preparation of starch (or derivatives) matrices are mostly based on methods like spray drying, jet cooking and emulsion cross-linking (Mauro, 1996; Qi & Xu, 1999; Shahidi & Han, 1993). These methods, however, have a number of disadvantages such as environmental pollution, high-energy costs and safety concerns. Extrusion, as an example of a continuous process for the preparation of starch based systems, is a cost-effective and environmentally friendly technology. Therefore extrusion processing is an attractive method to encapsulate a great variety of bioactive substances in starch matrices (Bergsma & Wierik, 1997; Carr, Wing & Doane, 1991; Chen & Jane, 1995; Doane, 1993; Trimnell & Shasha, 1988; Trimnell, Wing, Carr & Doane, 1991; Wierik, Eissens, Bergsma, Ardens-Scholte & Lerk, 1997; Wing, Maiti & Doane, 1987). For the encapsulation of hydrophobic substances such as fragrances, flavours, herbicides and insecticides into starch matrices, emulsifiers are often used to stabilise the morphology of the two-phase system. To control and modify the properties of the matrix systems, among which the release characteristics and stability of the system, it is required that control over the dispersed phase morphology is achieved (Pothakamury & Barbosa-Cánovas, 1995; Yılmaz, Jongboom, Van Soest & Feil, 1999). An important characteristic of an emulsifier is its hydrophile–lipophile balance (HLB) value, which is the balance of the size and strength of the hydrophilic and lipophilic moieties of an emulsifier molecule. The lower the HLB value, the more hydrophobic the emulsifier is. The HLB characteristic of an emulsifier is an important parameter to optimise the stability and the size of the dispersed droplets in a two-phase system of immiscible liquids (Davis, 1994).

In a previous study we have demonstrated that addition of glycerol as a plasticiser of starch had a significant effect on the dispersed phase morphology of sunflower oil composite films prepared by casting. It was observed that smaller sized dispersed oil droplets were formed with increasing amounts of glycerol. Since the viscosity of both phases remained

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Table 1
The composition of the premix formulations (all formulations contained 6.06 kg of native potato starch, 1 kg H_2O and 1 kg glycerol). The percentages are given in w/w on dry starch basis

Emulsifier	Emulsifier (%)	HLB value
Tween 20	2	16.7
Tween 40	2	15.9
Tween 60	2	14.9
Tween 80	2	15
Span 20	2	8.6
Span 40	2	6.7
Span 60	2	4.7
Span 80	2	4.3
Blank	–	0[a]
Tween 80/Span 80	0.4/1.6	7[b]
Tween 80/Span 80	1.0/1.0	10[b]
Tween 80/Span 80	1.6/0.4	13[b]

[a] Blank sample does not contain an emulsifier and the HLB value is arbitrarily set at 0.

[b] The HLB value of the mixture was calculated as follows: $X_aA + (1 - X_a)B = \mathrm{HLB}_{\mathrm{mixture}} = X_aA + (1 - X_a)B$ where X_a is the weight fraction of emulsifier a with the HLB value of A and B is the HLB value of emulsifier b.

unaffected, we concluded that the decreased droplet size was due to a decrease in the interfacial surface tension.

As a continuation of this work, we investigated the effect of HLB value of the emulsifier used and the processing conditions on the morphology of dispersed oil phase in a starch matrix prepared by extrusion. The aim of this study was to get insight into the relations between the processing parameters and the HLB value of the emulsifier on the one hand, and the morphology of the dispersed phase on the other.

Therefore, samples containing emulsifiers with different HLB values were prepared under different processing conditions. The obtained samples were analysed for their dispersed phase morphology using scanning electron microscopy (SEM). Sunflower oil was used as a model encapsulant and represents hydrophobic bioactive substances (Yılmaz et al., 1999).

2. Materials and methods

2.1. Materials

Native potato starch (17.5% moisture content) was purchased from Avebe, The Netherlands. Glycerol (density 1.26 g/ml) was purchased from Chemproha Chemicals Distributors BV, the Netherlands. Tweens (20, 40, 60, 80) and Spans (20, 40, 60, 80) which were applied as emulsifiers and the dye (FD&C Red No. 2, colour index no. 16185) which was used as a tracer for determination of the residence time, were purchased from Sigma Aldrich. Sunflower oil was a commercial product (De Burg BV, The Netherlands).

2.2. Processing and analysis

2.2.1. Premix preparation

The premixes (formulations fed into the extruder) were prepared as follows:

Ingredients for the premix were weighed and placed in the container of a bare varimixer in the following order; 6.06 kg of native potato starch, 1 kg of water, 1 kg of glycerol and 0–0.1 kg of emulsifier (or emulsifier mixture). The premix was obtained by mixing these ingredients at room temperature, for 10 min using a spiral mixing device coupled with the varimixer. The compositions of the different formulations are given in Table 1. One premix was

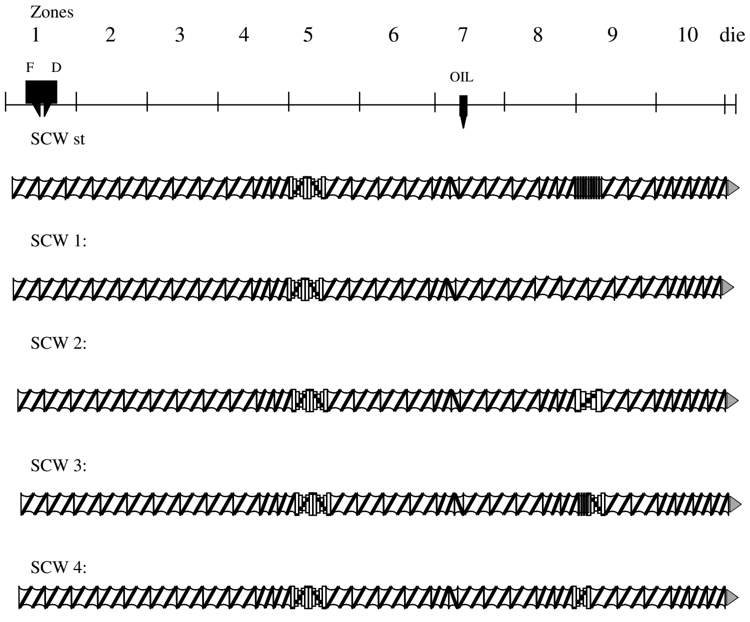

Fig. 1. Screw configurations.

Table 2
Extrusion of the blank premix formulations (Table 1) under different processing conditions

Condition	Screw	Throughput (kg/h)	rpm	T_{set} (°C) zones										
				1	2	3	4	5	6	7	8	9	10	Die
1	St	2.6	100	20	100	100	100	100	100	100	95	90	85	80
2	St	2.6	150	20	100	100	100	100	100	100	95	90	85	80
3	St	2.6	200	20	100	100	100	100	100	100	95	90	85	80
4	St	2.6	250	20	100	100	100	100	100	100	95	90	85	80
5	St	2.6	300	20	100	100	100	100	100	100	95	90	85	80
6	St	1.6	100	20	100	100	100	100	100	100	95	90	85	80
7	St	1.9	100	20	100	100	100	100	100	100	95	90	85	80
8	St	3.3	100	20	100	100	100	100	100	100	95	90	85	80
9[a]	St	2.6	100	20	100	100	100	100	100	100	95	90	85	80
10[a]	St	2.6	150	20	100	100	100	100	100	100	95	90	85	80
11[a]	St	2.6	200	20	100	100	100	100	100	100	95	90	85	80
12	St	2.6	100	20	85	85	85	85	85	85	80	75	70	65
13	St	2.6	100	20	115	115	115	115	115	115	110	105	100	95
14	Scw1	2.6	100	20	100	100	100	100	100	100	95	90	85	80
15	Scw2	2.6	100	20	100	100	100	100	100	100	95	90	85	80
16	Scw3	2.6	100	20	100	100	100	100	100	100	95	90	85	80
17	Scw4	2.6	100	20	100	100	100	100	100	100	95	90	85	80

[a] Extrusion without the die-head present.

prepared without an emulsifier (further indicated as 'blank' premix).

2.2.2. Extrusion of premixes

Extrusion experiments were performed using a twin screw, co-rotating self wiping extruder (Berstorff, $D = 25$ mm, $L = 40D$). A pre-die ($l = 50$ mm, $w = 10$ mm) and a die-head with two circular die-holes ($\varnothing = 3.2$ mm), were used.

For the first set of experiments (to investigate the effect of HLB of the emulsifier on the dispersed phase morphology), the different formulations with and without emulsifier(s) were introduced into the extruder via the feeder (K-tron screw feeder: $D = 5$ cm, at 50 rpm), at the inlet of the extruder (25–30°C). The gelatinisation of the starch matrix was allowed between the first and the seventh zone of the extruder. The applied 'standard' screw configuration is represented in Fig. 1 (SCW st). The set temperatures of the barrel were 20, 100, 100, 100, 100, 100, 100, 95, 90, 85, 80°C for the zones 1–10 and the die, respectively. Sunflower oil was injected with a piston pump (Pro Minet Verder BV, Germany) at the seventh zone. The amount of oil that was added was measured continuously during processing and was kept constant at 5% weight on dry starch basis. During the experiments the screw speed of the extruder was kept constant at 100 rpm. The throughput was 2.6 kg/h.

For the second set of experiments, 'blank' premixes were used to evaluate the effects of the following processing parameters on the dispersed phase morphology (Table 2):

- the screw speed was varied (conditions 1–5);
- extrusion without a die-head (conditions 9–11);
- the throughput was varied (conditions 1 and 6–8);
- different set temperatures of the barrel were applied (conditions 1, 12 and 13);
- different screw configurations (Fig. 1) were used (conditions 1 and 14–17).

The melt temperature, die pressure (both measured just before the die), throughput and the torque (%) were constantly registered during the processing.

2.2.3. Specific mechanical energy input

The specific mechanical energy (SME) was calculated according to the following equation (Guha, Ali, & Bhattacharya, 1997):

$$\mathrm{SME} = (\mathrm{rpm} \times \%\mathrm{torque} \times P_{\max})/(\mathrm{rpm}_{\max} \times 100 \times \mathrm{throughput}) \qquad (1)$$

For the extruder used, the highest possible screw speed ($\mathrm{rpm}_{\max}$) and the maximum power ($P_{\max}$) are 550 rpm and 10.5×10^3 J/s, respectively.

2.2.4. Sampling

When the process was steady, i.e. when processing variables such as torque and die pressure were constant (variation less than 5%) for at least 20 min, samples in which no oil was dispersed and samples with oil were collected at the die for 5 min. For each composition, five different samples were collected with intervals of 20 min. The residence time was measured using a tracer dye. All samples were stored in a conditioned room (20°C and 30% RH) prior to further analysis.

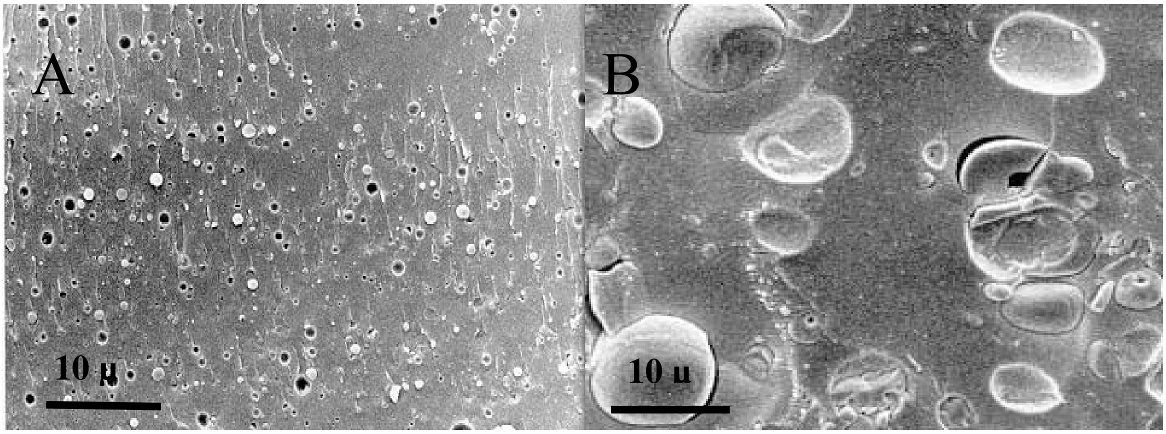

Fig. 2. SEM photographs of fractured surfaces of starch–oil composite extrudates. (a) Prepared using Tween 80 in the formulation. (b) Prepared with blank premix (see Table 1).

2.2.5. Dispersed phase morphology and particle size distribution (PSD)

The dispersed phase morphology of the samples was analysed by SEM. The samples were fractured cryogenically and cross-sections were analysed as described previously (Yılmaz et al., 1999).

The SEM photos were digitised and processed for particle size analysis by using image analysing software (Image pro-plus). The data were converted into Excel 5.0 (Microsoft) in order to calculate their particle size distributions. Average particle diameters ($n > 200$, number mean $D(1,0)$ and volume mean $D(3,0)$) and the polydispersity index ($D(3,0)/D(1,0)$) were calculated as described by Edmundson (1967).

2.2.6. Contact angles of sunflower oil with starch films

Starch extrudates (without oil) with different emulsifiers were compression moulded at 100°C at 20 bar pressure. The obtained smooth films were stored (60% RH, 20°C) until a constant weight was reached. Contact angle measurements were performed by means of a videotape technique, using a sessile drop method. The substrate (starch film) was placed on the sample stage equipped with a camera (VCA-2500™ camera). A droplet of sunflower oil (4 μl) was introduced onto the surface of the starch film using a syringe. Next, an image was captured of the sunflower oil droplet. The captured image was used for determination of the contact angle of sunflower oil on the substrates using the SE-2000 surface energy software package. The measurements were repeated five times for each substrate and average values were calculated.

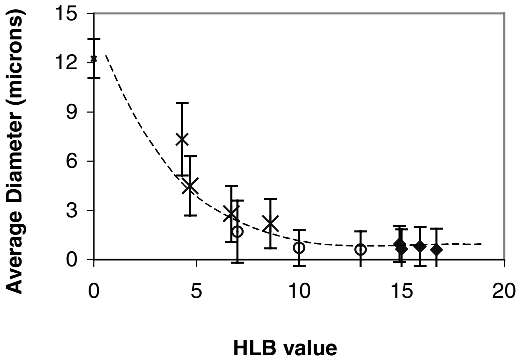

Fig. 3. Number mean diameters ($D(1,0)$) of starch–oil extrudates containing: Spans (×); Tweens (◆); mixtures of Tween and Span (○); no emulsifier (blank (■)) as a function of HLB value. Bars represent polydispersity index.

3. Results and discussion

3.1. Effect of the HLB value on morphology of the dispersed phase

3.1.1. SEM analysis of the dispersed phase morphology

Typical SEM photos of starch/sunflower oil matrices obtained by extrusion are given in Fig. 2. It is obvious that the use of an emulsifier resulted in a substantial reduction in the size of the dispersed oil droplets in comparison with matrices prepared without emulsifier.

Fig. 3 gives the relation between the number mean diameter $D(1,0)$, of the dispersed oil droplets as a function

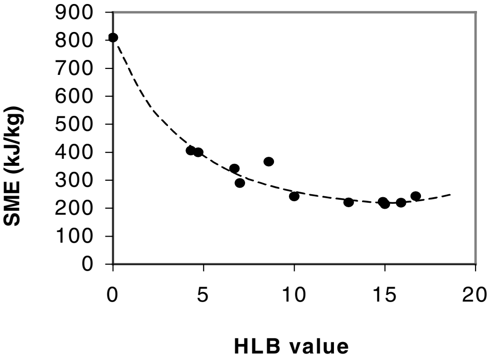

Fig. 4. The specific mechanical energy as a function of the HLB value of the emulsifier.

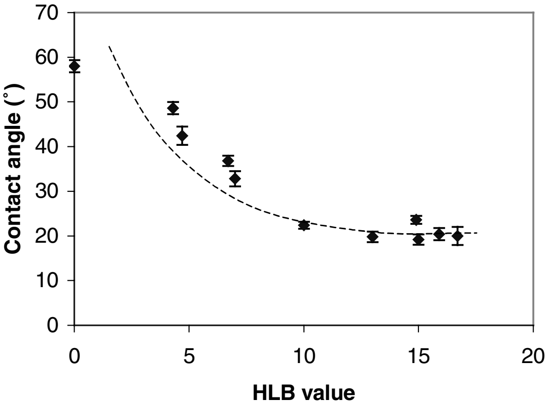

Fig. 5. Contact angle of sunflower oil droplet on starch films as a function of HLB value of the emulsifier (bars represent standard deviation).

of HLB value of the emulsifier. It can be seen that with increasing HLB value, the average particle size decreased. Especially in the HLB range 0–10, a strong reduction in average droplet diameter occurred.

3.1.2. *Effect of HLB value on the processing variables*

In comparison with a 'blank' premix, the extrusion of premixes with emulsifier resulted in a substantially lower torque value (31 and 13–21%, respectively). Furthermore, it was observed that the torque value decreased from 21 to 13% with increasing HLB value of the emulsifier. The specific mechanical energy (calculated using Eq. (1)) as a function of the HLB value of the emulsifier is given in Fig. 4. It can be seen that the SME decreased with increasing HLB value of the emulsifier, especially in the HLB range from 0 to 10 (Fig. 4). We demonstrated that within the same range of HLB values, the particle size of the dispersed oil droplets decreased (Fig. 3). This means that with increasing HLB, the interfacial surface increases, which in turn would be associated with an increase in SME provided that the interfacial energy between the phases is constant (Luzinov, Xi, Pagnoulle, Huynh-Ba, & Jérôme, 1999). However, the opposite was observed (Fig. 4). A possible explanation is that with increasing HLB of the emulsifier, the interfacial free energy between the two phases decreases and the formation of the dispersed phase requires therefore less energy.

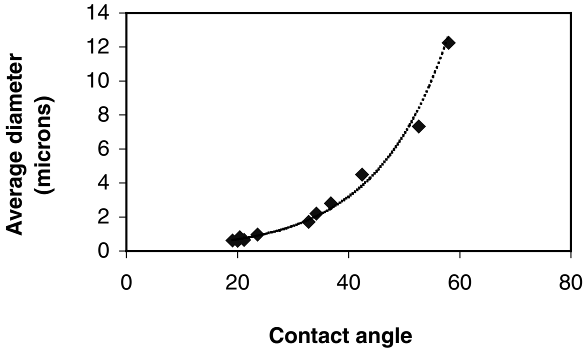

Fig. 6. Number mean diameters ($D(1,0)$) as a function of contact angle of oil on starch films with different emulsifiers.

3.1.3. *Contact angle measurements*

As the interfacial surface tension between sunflower oil and starch melt could not be measured directly during extrusion, post extrusion contact angle measurements were used as a measure of the interfacial surface tension between the two phases (Kinloch, 1990; Kwok & Neumann, 1998; Lawton, 1995; Lucianni, Champagne & Utracki, 1996; Wu, 1969). Contact angle values of sunflower oil on compression moulded starch samples with different compositions as a function of HLB value are shown in Fig. 5. As can be seen, the contact angle of sunflower oil on starch films showed a significant decrease with increasing HLB value of the emulsifier. When the results of Figs. 3 and 5 are combined to yield Fig. 6, it is shown that the average diameter of the oil droplets increases with the contact angle. This demonstrates that the interfacial free energy between the starch and oil phase dominates the formation of the dispersed phase morphology.

3.2. *The effect of process parameters on morphology of the dispersed phase*

The effect of the processing variables on the morphology of the dispersed phase was evaluated using blank premix formulations (Table 1).

3.2.1. *Screw speed*

A remarkable decrease in average diameters was observed at a constant throughput (2.6 kg/h), with increasing screw speed (Table 3). It was seen that the die pressure, the torque and the residence time decreased while the SME increased with increasing screw speed. There was no effect observed of screw speed on the melt temperature. The decrease in the die pressure, torque and the residence time at higher screw speeds can be explained by the reduced degree of fill (Graaf, Rohde & Janssen, 1997; Jager, van Zuilichem, Stolp & van't Riet, 1989; Jager, van Zuilichem & Stolp, 1992; Yacu, 1993), in combination with a reduced melt viscosity due to shear thinning behaviour of the starch melt (Chang & Halek, 1991; Della Valle, Boché, Colonna & Vergnes, 1995). This means that the increasing SME, which facilitates the creation of more interface between the starch melt and the oil phase, and the lower degree of fill in the extruder are the dominating factors to reduce the average size of the dispersed oil droplets.

3.2.2. *Extrusion with the pre-die*

In order to evaluate the effect of degree of fill, based on the previous results, the die-head was removed to obtain processing conditions with lower resistance at the die exit. In this way, the material could flow out more easily, which resulted in a decrease of the degree of fill in the extruder.

Table 3
Effect of screw speed on the processing variables and the dispersed phase morphology

Screw speed	Die pressure (bar)	Melt temp. (°C)	Torque (%)	SME (kJ/kg)	Res. time (s)	Mean size (μm)	
						D(1,0)	D(3,0)
100	30	97	31	819	480	12.3	15.3
100[a]	1	97	31	819	290	7.6	9.6
150	26	98	27	1070	430	8.6	12.3
150[a]	1	97	27	1070	270	6.0	8.8
200	15	98	24	1268	380	6.5	10.4
200[a]	1	97	24	1268	230	5.8	8.5
300	12	98	20	1586	330	3.3	4.4

[a] Extruded without the die-head present.

It was observed that processing with only the pre-die (die-head not present) resulted in a decrease of the average size of the dispersed oil phase, especially at low screw speeds (100 and 150 rpm; Table 3). As the SME was constant, the decrease of the particle sizes can therefore be attributed to the lower degree of fill, which apparently facilitated the process of breaking down of the oil droplets at the screw tips.

3.2.3. Throughput

When the throughput was increased, an increase in the average size of the oil droplets was observed (Table 4). It was observed that, the residence time and the SME substantially decreased especially in the range between 2.6 and 3.3 kg/h. Obviously, increasing the throughput resulted in an increased degree of fill, as indicated by the increasing die pressure. The material received less mechanical energy (SME) with increasing throughput, resulting in an increase in the particle size of dispersed oil droplets, fully in accordance with the previous findings.

3.2.4. Barrel temperature

An increase in the barrel temperature resulted in an increase in the melt temperature and a decrease of the size of dispersed oil droplets in the starch matrix (Table 5). As a result of increasing melt temperature, the interfacial tension between the starch phase and oil phase decreased favouring the formation of smaller oil droplets (Aveyard, Binks, Lawless & Mead, 1985). In addition, the viscosity ratio ($\eta_{\text{starch}}/\eta_{\text{oil}}$) decreased as the viscosity of the oil phase is only slightly reduced (Abramovič & Klofutar, 1998), while there is a strong reduction in the viscosity of the starch phase in the temperature range (85–115°C) of interest (Chang & Halek, 1991; Svegmark & Hermansson, 1991; Swinkels, 1985; Willett, Jasberg & Swanson, 1995; Zobel, 1984). The decreasing viscosity of the melt resulted that the material could flow out easier which in turn resulted in a decrease in the pressure build-up before the die (Table 5). A longer residence time, in this case, was not associated with higher degree of fill, since the residence time is also a function of the melt viscosity (Ruyck, 1997). Finally, the SME decreased with increasing temperature, which normally results in the formation of larger oil droplets when the other processing parameters are not affected. Obviously, the factors, which reduce droplet size (reduced viscosity and interfacial tension), have a stronger contribution to the formation of the dispersed phase than the factor which increases the droplet size (SME).

3.2.5. Screw configuration

The effects of the different screw configurations (Fig. 1) on the dispersed phase morphology and processing variables are given in Table 6. All screw configurations had small pitch transport elements towards the die (zone 10) which were required for the development of pressure to overcome the resistance at the die. The standard screw configuration had a low shear, mixing element (dispersive mixing discs), which facilitates the dispersive mixing in zone 9 (length: 37.5 mm). In contrast to the standard screw configuration, screw configuration 1 consisted only of a large and small pitch transport elements (zone 10). Screw configuration 2 was different from the others, since it had a positive large

Table 4
Effect of throughput on the process variables and the dispersed phase morphology

Throughput (kg/h)	Die pressure (bar)	Melt temp. (°C)	Torque (%)	SME (kJ/kg)	Res. time (s)	Mean size (μm)	
						D(1,0)	*D*(3,0)
1.6	17	98	20	859	690	5.8	15.3
1.9	24	98	23	820	570	10.0	15.3
2.6	30	97	31	819	480	12.3	15.3
3.3	37	98	30	620	150	24.3	46.5

Table 5
Effect of barrel temperature on the process variables and the dispersed phase morphology

Barrel temp.	Die pressure (bar)	Melt temp. (°C)	Torque (%)	SME (kJ/kg)	Res. time (s)	Mean size (μm)	
						D(1,0)	*D*(3,0)
Low	37	72	34	900	370	22.8	31.1
Medium	30	97	31	819	480	12.3	15.3
High	17	115	23	610	540	6.5	10.4

Table 6
Effect of screw configuration on the processing variables and the dispersed phase morphology

Screw configuration	Die pressure (bar)	Melt temp. (°C)	Torque (%)	SME (kJ/kg)	Res. time (s)	Mean size (μm)	
						D(1,0)	*D*(3,0)
St[a]	30	97	31	819	480	12.3	15.3
1	23	98	31	819	180	35.6	53.4
2	26	97	23	600	180	19.3	29.2
3	24	98	24	620	180	16.5	27.2
4	26	98	22	580	180	18.6	27.1

[a] Standard screw configuration.

pitch kneading element ($l = 37.5$ mm) in the 9th zone. This element is known to apply medium shear to the material, which facilitates mixing (Yacu, 1993). In screw configuration 3, the low shear mixing element ($l = 22.5$ mm) similar to the one in the standard screw configuration was combined with a high shear mixing element (small pitch, reverse kneading, $l = 25$ mm) in zone 9. Screw configuration 4 was rather comparable with the screw configuration 2 and had a positive, short pitch, kneading element incorporated in the 9th zone. This element provides a better conveying efficiency and distributive mixing efficiency than a larger pitch element.

The average diameter of the dispersed oil droplets obtained was the biggest with the screw configuration 1 (Table 6). With this screw configuration, the SME had a similar value and the residence time was less when compared to the standard screw configuration. With the standard screw configuration, although the SME was comparable with screw configuration 1, the observed average droplet size of oil was the smallest one (Table 6). This is probably due to the presence of the mixing element. It can be seen in Table 6 that the use of screw configuration 3 resulted in larger sized droplets when compared with the standard screw configuration. This can be explained by the lower SME values and by the shorter dispersive mixing element than the one incorporated in the standard screw. Screw configurations 2 and 4 resulted in similar average sizes of the oil (Table 6) which can be explained by the comparable processing variables.

4. Conclusions

The results presented in this paper demonstrate that the morphology of the dispersed phase of a hydrophobic liquid in a starch matrix via extrusion is dependent and can be tailored by both the formulation parameters and the processing conditions.

It was demonstrated that with increasing HLB value of the emulsifier (or mixtures of emulsifier) in the formulations resulted in a reduced size of the dispersed oil droplets. We showed that the size reduction of the dispersed phase was due to the interfacial surface tension that plays a dominant role in the creation of the morphology during extrusion if the processing conditions are kept constant.

Processing parameters such as screw speed, presence of die-head, throughput, melt-temperature and especially the screw configuration, also play an important role in the development of the dispersed phase morphology.

Presently, we are evaluating the release of volatile compounds from starch/oil two-phase systems with different morphologies and compositions.

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