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Effect of glycerol on the morphology of starch–sunflower oil composites

G. Yılmaz*, R.O.J. Jongboom, J.J.G. van Soest, H. Feil

ATO-DLO, P.O.Box 17, 6700 AA Wageningen, The Netherlands

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Abstract

The presented study involves the encapsulation of sunflower oil in starch by casting emulsions of oil in aqueous starch solutions. Glycerol was used as a plasticizer and lecithin was used as an emulsifier, to improve the emulsion stability. Increasing glycerol concentration in the samples resulted in different dispersed phase morphologies in the starch–sunflower oil composites. It was observed that increasing glycerol concentration resulted in a decrease in the particle sizes and polydispersity of the oil droplets. The two determining parameters on the formation of the dispersed phase during emulsification; viscosity and interfacial tension between two phases, were investigated to evaluate the effect of glycerol on the system. Since glycerol was found not to affect the viscosity of the aqueous starch phase, it was concluded that glycerol affects the dispersed phase morphology due to its effect on interfacial tension between the oil and aqueous starch phase, during emulsification. © 1999 Elsevier Science Ltd. All rights reserved

Keywords: Starch–sunflower oil composites; Glycerol; Lecithin; Morphology; Encapsulation

1. Introduction

Encapsulation is a process for entrapping or coating a material within another material. This technology is applied for a number of reasons ranging from protection, stabilization, obtaining a controlled or targeted release, masking the core material properties, to simply convert a product from a liquid into a solid form (Shahidi and Han, 1993; Risch, 1995; King, 1995).

Matrix materials used for encapsulation are usually film forming materials that can be selected from a wide variety of natural or synthetic polymers or oligomers, depending on the core material and desired characteristics of the product. Starch is a material, that has a large potential for encapsulation purposes (Kenyon, 1995; Shahidi and Han, 1993). It is one of the most abundant biopolymers on earth, it is cheap, fully biodegradable and edible. Amylopectin and amylose are the main components of starch. Amylose is able to form complexes with different kinds of substances such as fatty acids, ketones, amines, salts, alcohols (Bhatnagar and Hanna, 1994; Hulleman et al., 1996), which provides a powerful tool for encapsulating a compound effectively.

Starch processing can be performed using techniques such as extrusion, steam jet cooking or spray drying. When processing starch for encapsulation purposes, plasticizers are necessary to optimize mechanical properties and diffusivity characteristics. Glycerol is often used as a plasticizer for starch. Besides transition temperatures, mechanical and diffusivity parameters (Leslie et al., 1991; Shogren et al., 1992; Van Soest et al., 1996; Arvannitoyannis et al., 1997; St.Pierre et al., 1997), glycerol affects development of crystallinity due to its hygroscopic character (Van Soest and Knoren, 1997). This provides different structural characteristics for the starch matrix (Karel, 1987; Morris, 1990).

Encapsulation of oils enables the incorporation of additional amounts of hydrophobic materials and is representative for many applications of encapsulation (Matsuno and Adachi, 1993; Fanta and Eskins, 1995; Eskins and Fanta, 1996; Eskins et al., 1996; Knutson et al., 1996; Poncelet and Neufeld, 1996). When a hydrophilic matrix such as starch is used, stability is mainly dependent on mechanical properties (brittle or rubbery), and the diffusivities. The release mechanism in such a system is controlled by diffusion in three subsequent steps. These steps are dissolution to the matrix, diffusion through the matrix and transport from the matrix into the environment (Pohakamury and Barbosa-Cánovas, 1995; Reineccius, 1995).

Diffusivity parameters of a matrix material are determined by crystallinity (barriers to diffusion) of the matrix, mechanical state (glassy or rubbery), solubility of the encapsulant, and moisture content (Washington, 1996).

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* Corresponding author

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All these determining parameters can easily be adjusted by changing the glycerol content of the starch matrix. However, dissolution of an encapsulant into the matrix influences the concentration gradients within the matrix as a result of the resistance at the interfacial layer. The net flux of encapsulant is, therefore, affected by the area that is available for mass transfer (interfacial area). The amount of interfacial surface area, in turn, is determined by the dispersed phase morphology. These considerations indicate that the dispersed phase morphology plays an important role in two out of three rate determining steps for diffusion determined controlled release systems (Baker and Lonsdale, 1974). However, the effect of glycerol on the dispersed phase morphology is unknown.

In this paper a model study is presented in which sunflower oil is encapsulated in a starch matrix. As a processing method, a solution casting procedure was chosen. Sunflower oil was used as a non-volatile model substance. It was first emulsified in the aqueous starch phase. The emulsions were then cast and dried towards films. This method allowsa variation in the amount of glycerol and is easily applicable.

The dispersed phase morphology of the composite films was analysed using scanning electron microscopy. It was assumed that the dispersed phase, created during emulsification, was preserved during drying of the solutions. Viscosities of the aqueous starch solutions and interfacial tension between the aqueous and oil phase were investigated, as they were expected to be the dominant parameters that affect the morphology of the dispersed phase (Walstra, 1983, 1991).

The aim of this study is to investigate and evaluate the effects of glycerol on the morphology of the dispersed phase, as the morphology of the dispersed phase can potentially provide tools for adjusting the release behaviour of controlled release systems effectively.

2. Materials and methods

2.1. Materials

Native potato starch was purchased from Avebe, The Netherlands. The water content was 17.4%. Chemically pure glycerol (density 1.26) was purchased from Chemproha Chemicals Distributors B.V., The Netherlands. Soy lecithin (Topcithin 50, Lucas Meyer) was applied as an emulsifier. The applied sunflower oil, was a commercially available, edible oil (De Burg B.V., The Netherlands).

2.2. Sample preparation

The samples were prepared by weighing 10.0 g of native potato starch (8.26 g dry basis) in a 600 ml glass beaker and adding 200 ml of demineralized water. Subsequently, additional glycerol was added to the water–starch mixtures in concentrations of 0%, 12%, 24%, 36%, 48% and 73% (w/w), respectively, on dry starch basis.

The gelatinization of the starch pastes was performed by heating the mixtures on a hot plate under continuous stirring. A temperature gradient of 2°C min^{-1} was applied. Stirring was performed with a mechanical propeller stirrer (IKA - Rührwerke RW 20) at a constant speed of 650 rpm. During the gelatinization procedure, the beaker was covered with aluminium foil in order to avoid evaporation of water. The final temperature of the starch slurries was 85°C.

The gelatinized starch pastes were cooled down to 70°C, before the other components were added, in order to prevent evaporation of water. The lecithin (10% w/w of oil) was mixed with 3 g of sunflower oil, which was used in all experiments, prior to emulsification.

The starch–oil mixtures were stirred for 5 min at a stirring speed of 650 rpm. The oil in starch emulsions were subsequently cast into 12 × 12 cm polystyrene boxes. The samples were dried under controlled conditions (20°C and 30% RH), until the films reached constant weight. Prior to analysis, all the samples were kept in a conditioned room (20°C, 30% RH) until they were analysed. Each sample was prepared in triplicate.

2.3. Dispersed phase morphology as determined by SEM

The starch–oil films were analysed, using a Phillips 535 scanning electron microscope (SEM). The samples were broken cryogenically by putting the sample material on a metal block, which was placed in a liquid nitrogen bath. The films were gently broken in order to investigate the cross-sections of the samples. A thin layer of gold was sputter coated onto the samples under vacuum. The samples were magnified up to 5000 times and photographs were taken at magnifications 250×, 500×, 1000× and 5000×.

2.4. Determination of the particle size distribution (PSD)

The 500 × and 250 × magnified SEM pictures of the samples were digitized using a HP Scan Jet 4c (Hewlett Packard, USA) scanner. The digitized pictures were analysed, using image-analysing software [Image pro (Plus version 2.0 for Windows 95, Media Cybernetics L. P., USA]. The diameter distributions of the droplets (particles) in the starch matrices were determined for all samples in triplicate. The obtained data were converted into Excel 5.0 format and particle size distributions (PSD) were plotted. For a good description of the distribution, standard deviation values, arithmetic average and mode diameters were calculated. The mode diameter passes through the peak of the distribution line where the frequency is highest. Arithmetic average diameter is defined by:

$$d_{\mathrm{a}} = \sum_n d/n \tag{1}$$

where n represents the number of counted oil droplets.

σ_{a} is the arithmetic standard deviation defined by:

$$\sigma_{\mathrm{a}}^2 = \sum_n (d - d_{\mathrm{a}})^2/n \tag{2}$$

Calculation of the total interfacial surface area for samples was performed using average diameters. The analysed surface area in total was 900 000 μm^2 for each sample. This area was considered to be representative for each sample.

2.5. Determination of the interfacial tension

Interfacial tensions were measured using a tensiometer (model K6, Krüss), fitted with a platinum ring attachment. The measurements were carried out at 70°C which is identical to the temperature during the emulsification of the oil in the starch paste.

The starch–glycerol–water phase and oil phase were prepared as described in the sample preparation. In order to perform interfacial tension measurements, the platinum ring was first placed on the starch paste, and subsequently the oil phase was added on top of it, using a 10 ml pipette. All measurements were performed in triplicate. The tensiometer determined the maximum force to overcome the interfacial tension. The apparent O/W interfacial tension (γ^*) was converted to absolute values (γ, mN m^{-1}) using:

$$\gamma = F\gamma^* \qquad (3)$$

Values of the correction factor F calculated by using the formula:

$$F = 0.725 + (0.4036 \times 10^{-3} \times (\gamma^*/D - d) + 0.0128)^{0.5} \qquad (4)$$

with $D - d$ being the density difference between the two phases (Harkins and Jordan, 1930; Tadros and Vincent, 1983).

2.6. Rheological examination

For determination of the rheological properties of the aqueous starch pastes, viscosity measurements were performed, using a Brookfield programmable rheometer (Model DV.III; Brookfield engineering laboratories Inc.). Rheocalc V1.01 (Microsoft Corporation) was used as a support program during the measurements. Of each solution an amount of 10 g was weighed into the sample holder. The viscosities of the samples were determined at 70°C at spindle speeds ranging from 20 to 100 rpm. The measurements were performed in triplicate.

For evaluation, the results of viscosity measurements were fitted to the Power Law, known as:

$$\Upsilon = kD^n \qquad (5)$$

where Υ is shear stress (N m^{-2}), k is consistency index (mPas), D is shear rate and n is the flow index (Evans and Haisman, 1979; Janas, 1991; Waniska and Gomez, 1992; Willet et al., 1995).

3. Results and discussion

3.1. Morphology analysis

Drying the emulsions, resulted in starch–oil composite films which did not exhibit any visible leaking of oil during the drying period.

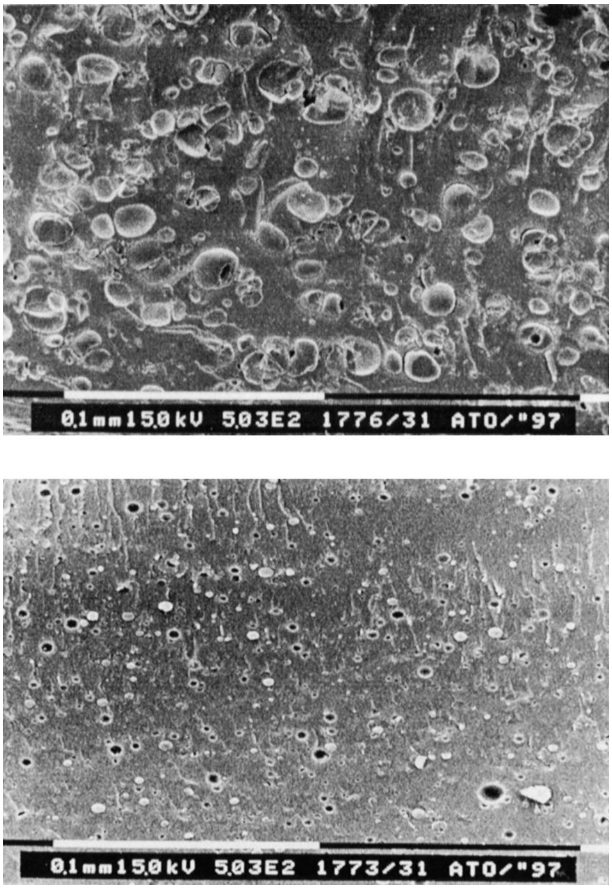

Fig. 1. SEM photos of the starch oil composite films (A — 36% glycerol; B — 73% glycerol).

Typical SEM photos of a fractured starch–oil composite film with 36% glycerol and 73% glycerol are shown in Fig. 1.

Morphological analysis by SEM showed that there were significant differences in the morphologies of the starch–oil composite films of different glycerol concentrations.

Higher glycerol concentrations resulted in smaller droplet diameters of oil dispersed in starch. The particle size distributions are shown in Fig. 2.

The average diameter of the oil droplets decreased from 130 μm with 0% glycerol to 7 μm with 73% glycerol. Higher glycerol concentrations led to a lower polydispersity. Average diameters and standard deviation values as a function of glycerol concentration are given in Table 1.

Consequently, the decrease of the sizes of the oil droplets lead to increasing interfacial surface area values. This increase of the interfacial surface can be seen in Fig. 3.

The differences in the interfacial surface area values are likely to affect the dissolution rate of the encapsulant into the matrix. A different dissolution rate is expected to affect

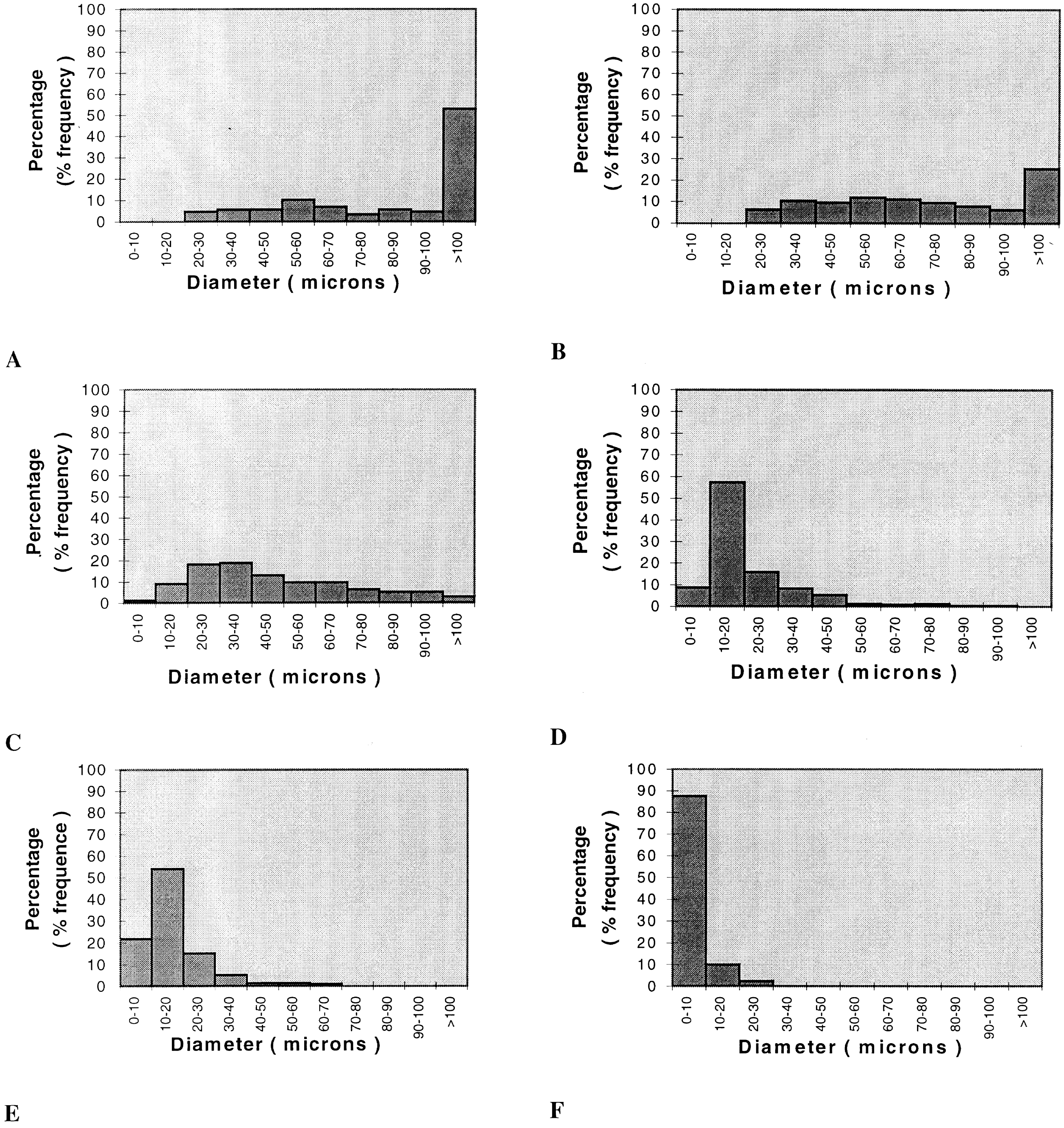

Fig. 2. Particle size distributions of the samples: A, 0% glycerol (% dry starch basis); B, 12% glycerol (% dry starch basis); C, 24% glycerol (% dry starch basis); D, 36% glycerol (% dry starch basis); E, 48% glycerol (% dry starch basis); and F, 73% glycerol (% dry starch basis).

the concentration gradient (driving force for mass transfer) of the encapsulant within the matrix in non-equilibrium conditions. The change in the concentration gradient can potentially cause changes in the release pattern of the encapsulant (Pohakamury and Barbosa-Cánovas, 1995; Reineccius, 1995; Washington, 1996). As a result, modification of the dispersed phase morphology and, accordingly, the release behaviour of a hydrophobic encapsulant in a starch matrix can be acheived by the use of glycerol.

3.2. Viscosity measurements

Viscosity measurements were performed on the aqueous starch solutions with different glycerol concentrations under several shear rates. The experimental data could satisfactorily be fitted to the power law equation. All aqueous starch pastes showed power law behaviour with a confidence of fit ranging between 97% and 99.5%. The power law parameters can be seen in Fig. 4.

Table 1
The effect of glycerol concentration on the polydispersity and the average diameter of oil droplets in starch–oil composites

Glycerol concentration (% dry starch)	Average diameter (μ)	Standard deviation
0	130	87
12	76	35
24	49	26
36	21	15
48	17	10
73	7	3

The changing glycerol concentration did not have any significant effect on the viscosities under the conditions as applied during this study.

However, there were fluctuations in the values of measured viscosities of the starch pastes. These fluctuations in the measurements can be explained by the fact that the temperature range over which the measurements were performed, was close to the peak viscosity of the gelatinization period. Additionally the temperature sensitive behaviour of potato starch is believed to contribute to the fluctuations (Svegmark and Hermansson, 1990, 1991; Kokini et al., 1992).

It is known from the literature that the viscosities of starch pastes are generally affected by the addition of glycerol (Janas, 1991) and glycerol influences the gelatinization temperature (Van Soest et al., 1996). However, in the presented study, the glycerol content is only a small percentage in the starch–glycerol–water complete system when compared with the water content. In such a system it is understandable that changes in glycerol concentration do not have significant effects on viscosity of the system.

It is of great importance to determine the viscosity of the aqueous starch pastes. The viscosity of the starch paste in the system gives information about mixing effects and the viscous stresses on the breaking of droplets of oil. As known from previous studies, it is one of the determining parameters for the formation of the dispersed phase during emulsification in the studied system (Walstra, 1983, 1991). Breaking of the droplets during emulsification results from shear effects in turbulent flow provided by a stirrer. The dispersed phase droplets are subjected to viscous stresses resulting from continuous phase (i.e. aqueous starch solution) viscosity (Schubert and Armbruster, 1989; Poncelet and Neufeld, 1996).

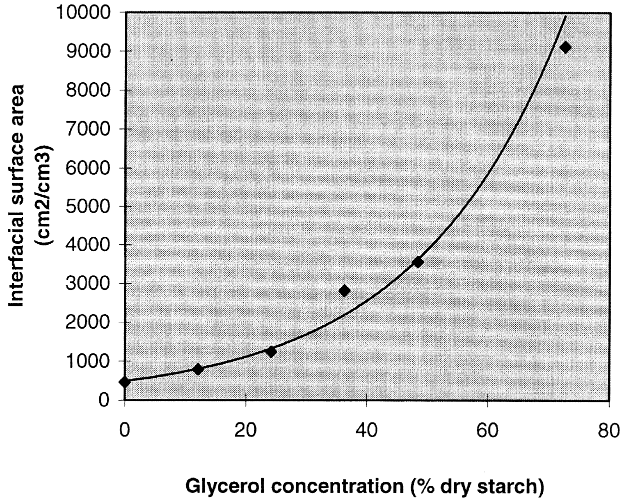

Fig. 3. Total interfacial area created as a result of changing glycerol concentration.

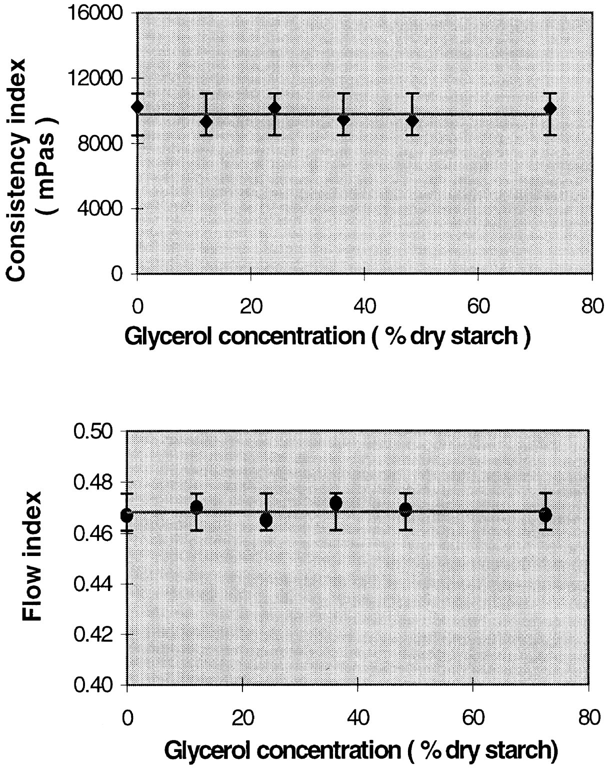

Fig. 4. Power law parameters.

Considering the results of the measurements, viscosities of the aqueous starch pastes were not a relevant parameter for the formation of different dispersed phases in the studied system, as the viscosities were not affected by the glycerol concentration.

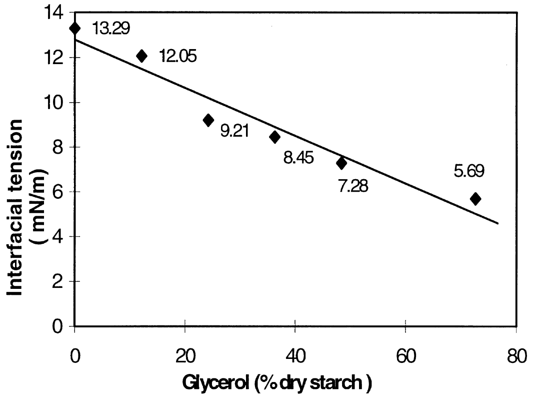

Fig. 5. Effect of glycerol concentration on interfacial tension.

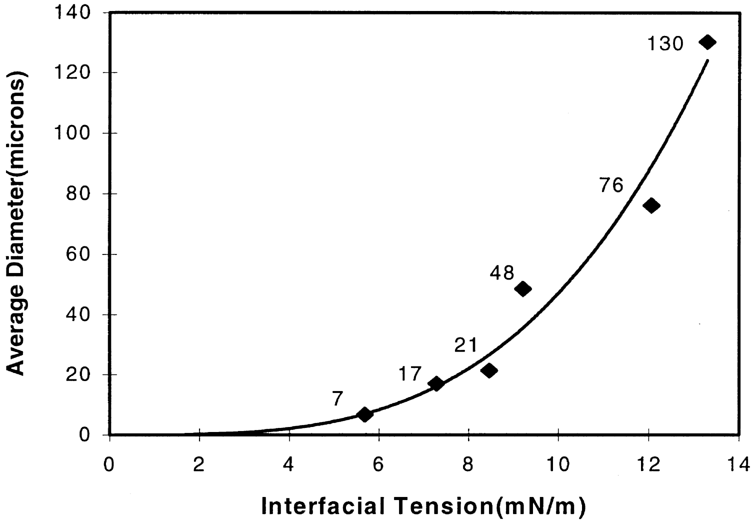

Fig. 6. Effect of interfacial tension on the average diameter.

3.3. Interfacial tension measurements

The interfacial tension decreases between the two phases which are the continuous phase (i.e. aqueous starch paste) and the dispersed phase (i.e. sunflower oil) with increasing glycerol concentrations. The relation between interfacial tension and the glycerol concentration is shown in Fig. 5.

The average diameter values of the dispersed oil in relation to the changing interfacial tension between aqueous starch pastes and sunflower oil can be seen in Fig. 6.

Apparently the morphology of the dispersed phase of the investigated system is determined by the interfacial tension between oil and the aqueous starch pastes. It is known from the literature that the creation of the dispersed phase and the size of the dispersed phase droplets are highly dependent on the interfacial tension between the continuous phase and the dispersed phase. Decrease in the interfacial tension makes it easier to break down the oil droplets into smaller ones (Becher, 1977; Rosen, 1989). The previous studies show that the repulsive forces between the dispersed phase droplets provided by the emulsifier (i.e. lecithin) contributes to the stabilization of the emulsion. The increase of the viscosity of the system due to decreasing temperature prevents the dispersed phase droplets from coalescing (Schubert and Armbruster, 1989).

Consequently, these results indicate that the responsible parameter for the formation of smaller oil droplets is the interfacial tension between two phases affected by glycerol. This gives the impression that glycerol acts as a co-emulsifier in the system.

During cooling down of the paste, an increased viscosity was observed. The increasing viscosity of the starch paste with the reduction of temperature in the starch paste contributes to the stability of the system in which further coalescence with time is prevented.

4. Conclusions

This model study on starch–oil composites showed that glycerol can be an effective parameter for controlling the morphology of the starch–sunflower oil composites.

The viscosity of the aqueous starch solutions was not affected by glycerol concentration. Consequently, the cause for the observed formation of droplets of different sizes was due to the change in interfacial tension between the oil and the aqueous starch phase at different glycerol concentrations. Apart from being a plasticizer for starch, the effect of glycerol on the creation of different morphologies in the investigated system was remarkable. It was concluded that glycerol acts as a co-emulsifier and provides an additional decrease in interfacial tension between the oil and aqueous phase.

These results indicate that glycerol is a tool in controlling the morphology of starch–oil composites and, accordingly, for controlling the release behaviour of an encapsulant from such matrices.

References

Arvannitoyannis, I., Bsomiadou, E., Nakayama, A., Aiba, S., & Yamamoto, N. (1997). Edible films made from gelatin, soluble starch and polyols. *Food Chem., 60 (4),* 593–604.

Baker, R.W., & Lonsdale, H.K. (1974). Controlled release: mechanisms and rates. In A.C. Tanquary & R.E. Lacey (Eds.), *Controlled release of biologically active agents* (pp. 15–71). New York: Plenum Press.

Becher, P. (1977). Theory of emulsions: stability. In E. Robert (Ed.), *Emulsions theory and practice* (pp. 94–149). New York: Krieger.

Bhatnagar, S., & Hanna, M.A. (1994). Extrusion for amylose–lipid complexing. *Cereal Chem., 71 (6),* 587–593.

Eskins, K., Fanta, G.F., Felker, F.C., & Baker, F.L. (1996). Ultrastuctural studies on microencapsulated oil droplets in agueous gels and dried films of a new starch–oil composite. *Carb. Polym., 29,* 233–239.

Eskins, K., & Fanta, G. (1996). Carbohydrate–oil composites useful in low fat foods, cosmetics, drugs and industrial applications. *Lipid Technol*. May, 53–57.

Evans, I.D., & Haisman, D.R. (1979). Rheology of gelatinized starch solutions. *J. Texture Stud.*, *10*, 347–370.

Fanta, G.F., & Eskins, K. (1995). Stable starch lipid compositions prepared by steam jet cooking. *Carb. Polym.*, *28*, 171–175.

Harkins, W.D., & Jordan, H.F. (1930). A method For the determination of surface and interfacial tension from the maximum pull on the ring. *J. Am. Chem. Soc.*, *82*, 1751–1773.

Hulleman, S.H.D., Helbert, W., & Chanzy, H. (1996). Single crystals of V amylose complexed with glycerol. *J. Biol. Macromol.*, *18*, 115–122.

Janas, P. (1991). Rheological studies on potato starch pastes at low concentrations. Part IV. *Starch/Stärke*, *43*, 172–175.

Karel, M. (1987). Encapsulation and controlled release of food components. In *Biotechnology and food processing, IFT Basis Symposium Series* (pp. 277–293). New York: Marcel Dekker.

King, A.H. (1995). Encapsulation of food ingredients. In S.J. Risch & G.A. Reineccius (Eds.), *Encapsulation and controlled release of food ingredients* (pp. 27–39). Washington, DC: American Chemical Society.

Kenyon, M.M. (1995). Modified starch, maltodextrin and corn syrup solids as wall materials for food encapsulation. In S.J. Risch & G.A. Reineccius (Eds.), *Encapsulation and controlled release of food ingredients* (pp. 43–49). Washington, DC: American Chemical Society.

Knutson, C.A., Eskins, K., & Fanta, G.F. (1996). Composition and oil retaining capacity of jet cooked starch oil composites. *Cabohydrates*, *73 (2)*, 185–188.

Kokini, J.L., Lai, L.S., & Chedid, L.L. (1992). Effect of starch structure on rheological properties. *Food Technol*. June, 124–139.

Leslie, R.B., Carillo, P.J., Chung, T.Y., Gilbert, S.G., Hayakava, K., Marousis, S., Saravacos, G.D., & Solberg, M. (1991). Water diffusivity in starch based systems. In H. Levine & L. Slade (Ed.), *Water relations* (pp. 365–389). New York: Plenum Press.

Matsuno, R., & Adachi, S. (1993). Lipid encapsulation technology. *Trends Food Sci. Technol.*, *4*, 256–261.

Morris, V.J. (1990). Starch gelation and retrogradation. *Trends Food Sci. Technol.*, *2*, 1–6.

Pohakamury, U.R., & Barbosa-Cánovas, G.V. (1995). Fundamental aspects of controlled release in foods. *Trends Food Sci. Technol.*, *6*, 397–406.

Poncelet, D., & Neufeld, R.J. (1996). Fundementals of dispersion in encapsulation technology. In R.M. Wijffels, R.M. Buitelaar, C. Bucke & J. Tramper (Eds.), *Immobilized cells* (pp. 47–55). Amsterdam: Elsevier.

Reineccius G.A. (1995). Controlled release techniques in the food industry. In S.J. Risch & G.A. Reineccius (Eds.), *Encapsulation and controlled release of food ingredients* (pp. 9–25). Washington, DC: American Chemical Society.

Risch, S.J. (1995). Encapsulation: overview of uses and techniques. In S.J. Risch & G.A. Reineccius (Eds.), *Encapsulation and controlled release of food ingredients* (pp. 3–7). Washington, DC: American Chemical Society.

Rosen, M. J. (1989). Reduction of surface and interfacial tension by surfactants. In *Surfactants and interfacial phenomena* (2nd ed). New York: Wiley.

Schubert, H., & Armbruster, H. (1989). Principles of processing and stability of food emulsions. In W.E.L. Spiess & H. Schubert (Eds.), *Engineering and food* (Vol. 1, pp. 185–205). London: Elsevier.

Shahidi, F., & Han, X.Q. (1993). Encapsulation of food ingredients. *Crit. Rev. Food Sci. Nutrition*, *33 (6)*, 501–547.

Shogren, R.L., Swanson, C.L., & Thompson, A.R. (1992). Extrudates of cornstarch with urea and glycols: structure/mechanical property relations. *Starch/Stärke*, *44*, 335–338.

St.Pierre, N., Favis, B.D., Ramsay, B.A., Ramsay, J.A., & Verhoogt, H. (1997). Processing and characterization of thermoplastic starch/polyethylene blends. *Polymer, 38 (3)*, 647–655.

Svegmark, K., & Hermansson, A.M. (1990). Shear induced changes in the viscoelastic behaviour of heat treated potato starch dispersions. *Carb. Polym.*, *13*, 29–45.

Svegmark, K., & Hermansson, A.M. (1991). Changes induced by shear and gel formation in the viscoelastic behaviour of potato, wheat and maize starch dispersions. *Carb. Polym.*, *15*, 151–169.

Tadros, T.F., & Vincent, B. (1983). Liquid–liquid interfaces. In P. Becker (Ed.), *Encyclopedia of emulsion technology* (Vol. 1, pp. 1–56). Wilmington, DE: Paul Becher.

Van Soest, J.J.G., Bezemer, R.C., & De Wit, D. (1996). Influence of glycerol on the melting of potato starch. *Ind. Crops Prod.*, *5*, 1–9.

Van Soest, J.J., & Knoren, N. (1997). Influence of glycerol and water content on the structure and properties of extruded starch. *J. Appl. Polym. Sci.*, *64*, 1411–1422.

Walstra, P. (1983). Formation of emulsions. In P. Becker (Ed.), *Encyclopedia of emulsion technology* (Vol. 1., pp. 58–125). Wilmington, DE: Paul Becher.

Walstra, P. (1991). Principles of emulsion formation. In J. Laven & H.N. Stein (Eds.), *The preperation of dispersions*, Preprints of the IACIS Conference, The Netherlands, pp. 77–92.

Waniska, R.D., & Gomez, M.H. (1992). Dispersion behaviour of starch. *Food Technol*. June, 112–123.

Washington, C. (1996). Drug release from microparticulate systems. In S. Benita (Ed.), *Microencapsulation: methods and industrial applications* (pp. 156–175). New York: Marcel Dekker.

Willet, J.L., Jasberg, B.K., & Swanson, C.L. (1995). Rheology of thermoplastic starch: effects of temperature, moisture content and additives on melt viscosity. *Polym. Engng Sci.*, *35 (2)*, 202–210.