Solid-State Emulsions: The Effects of Maltodextrin on Microcrystalline Aging

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INTRODUCTION

The physical stability of conventional emulsions is well-known (1). Several investigators (2–4) have attempted to develop emulsion systems that would allow for the storage of emulsions as solids. Additionally, the ability to prepare emulsions without the use of inherently problematic surfactants would represent a significant advancement of dispersion/emulsion technology. The solid-state emulsion system previously reported by Myers and Shively (5) represents such a system, in that the emulsion may be stored as a solid yet no emulsifying agent is utilized.

The emulsions described are prepared from solid-state emulsions prepared by previously reported methods (5,6). Without the aid of surfactants, O/W emulsions result upon the addition of an aqueous phase to the appropriately prepared solids. The particle size characteristics of these aqueous emulsions indicate a unimodal distribution of particles with an average droplet diameter of approximately 1.5 μm (7).

Although the test system has the distinct advantage of storage as a solid, in some cases, i.e., sucrose, the solid has been shown to be a metastable glass (6). Metastable systems undergo aging or transformation to the more stable or lower energy state as a function of time (8,9). Aging dramatically changes in the vicinity of the glass transition temperature due to increasing translational and rotational movements. Due to hindered molecular movements below the glass transition, molecules are slowed in attaining a lower energy state (10). The region of the glass transition temperature may be determined using differential scanning calorimetry (DSC) (11).

The use of polymers has been reported (8,9) to increase the glass transition temperature by providing an additional obstacle to molecular rearrangement. In contrast, residual water acts to reduce the glass transition temperature (6). In an effort to modify the stability of glass-like solid-state emulsions, maltodextrins were incorporated into the glass matrix. Maltodextrins are nonsweet, nutritive saccharide polymers that are comprised of D-glucose units linked by α-1-4 bonds having a range of dextrose equivalents, e.g., 5 to 18 (12). Maltodextrins were specifically chosen in this study because of (i) the ability to enhance compression characteristics within tablet formulations, (ii) the classification as generally recognized as safe (GRAS) by the FDA, (iii) the lack of inherent emulsifying properties, and (iv) the availability of solids with different surface properties, i.e., agglomerated and nonagglomerated. Different agglomeration states of maltodextrin were utilized to investigate if oil adsorbs to the surface of maltodextrin, in which case the surface properties of maltodextrin would be important.

In the present study, the feasibility of modifying the physical stability of solid-state emulsions with maltodextrins was evaluated. Due to the commercial availability of maltodextrins of two distinct surface properties, it was possible to explore the surface adsorption of oil as a rationale to explain the observed dispersion properties.

MATERIALS AND METHODS

Materials. Maltodextrins (see Tables I and II) were supplied by the Grain Processing Corporation (Maltrins, Muscatine, IA). Sucrose (reagent grade, MCB, Norwood, OH) and heavy mineral oil (USP, Fisher Scientific, Pittsburgh, PA) were used as supplied. Double distilled, deionized water was used throughout.

Preparation of Solid-State Emulsions. Solid-state emulsions were prepared using a procedure similar to that described previously (5–7). The procedure was modified by using variable amounts of maltodextrin (5 to 100%, w/w) as the matrix material in place of sucrose. The matrix material to oil ratio, on a per weight basis, was maintained at a constant 3.5:1 matrix:oil. Solid-state emulsions were stored at room temperature in desiccators containing calcium carbonate.

Differential Scanning Calorimetry. In all cases, a Perkin-Elmer DSC-7 (Norwalk, CT) was utilized. The calorimeter was equipped with an intracooler and a glove box. The

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Table I. Percentage Microcrystallinity with Respect to Concentration Using Nonagglomerated Maltodextrin with Various DE Values

Sample	DE No.	0	5	10	15	25	50	100
M-040	5	59.0	17.9	12.0	8.0	8.7	0.0	0.0
M-100	10	59.0	16.3	44.4	—[a]	—	0.0	0.0
M-150	15	59.0	55.9	6.5	7.0	10.0	0.0	0.0
M-180	18	59.0	19.7	8.1	26.3	11.7	2.5	0.0
Average		59.0	27.5	17.8	13.8	10.1	0.7	0.0
SE		0.0	9.5	9.0	6.3	0.8	0.6	0.0

[a] Percentage microcrystallinity was not recorded because samples were not prepared at this concentration.

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Table II. Percentage Microcrystallinity with Respect to Concentration Using Agglomerated Maltodextrin with Various DE Values

Sample	DE No.	0	5	10	15	25	50	100
M-440	5	59.0	60.1	11.0	5.1	6.3	0.0	0.0
M-500	10	59.0	72.8	13.1	29.3	—[a]	0.0	0.0
M-550	15	59.0	15.7	4.7	27.1	16.2	0.0	0.0
M-580	18	59.0	25.8	9.7	13.9	13.7	7.6	0.0
Average		59.0	47.7	9.6	19.0	12.1	1.9	0.0
SE		0.0	13.7	1.8	5.8	3.0	1.9	0.0

[a] Percentage microcrystallinity was not recorded because samples were not prepared at this concentration.

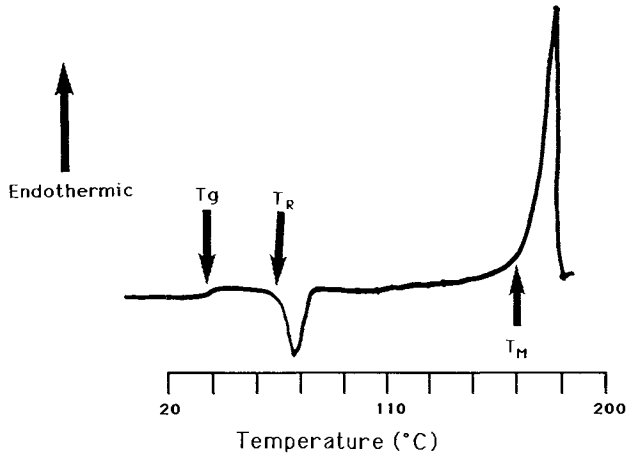

Fig. 1. Differential scanning calorimetry thermogram of a representative solid-state emulsion, comprised of 3.5:1 sucrose:mineral oil. T_g = 38°C; T_R = 56°C; T_M = 178°C.

sample compartment was purged with a continuous flow of nitrogen (USP) at 20 psi, while the glove box was purged at 2 psi. The calorimeter was calibrated daily with indium. Solids were weighed (3.0–9.0 mg), compressed, and sealed in aluminum sample pans (Perkin-Elmer, Norwalk, CT). All samples were evaluated 24 hr after preparation, from 0 to 200°C at a scanning rate of 10°C/min.

RESULTS AND DISCUSSION

The solids formed were dry "foam-like" materials with no residual oil observed. These solids have been shown previously, using X-ray diffraction, to be completely amorphous (6). A typical DSC thermogram of a solid-state emulsion (3.5:1 sucrose:mineral oil) is shown in Fig. 1. Characteristic features in Fig. 1 are identified as the glass transition temperature (T_g), recrystallization temperature ($T_{R,\ exothermic}$), and melting temperature ($T_{M,\ endothermic}$). If the heat of recrystallization (ΔH_R) is assumed to be equal but opposite in sign to the heat of melting (ΔH_C), the initial crystallinity of the sample before heating may be calculated (13). Due to X-ray diffraction indicating that there is no detectable crystallinity before heating, the initial crystallinity detected by the above procedure (13) as described in this report is referred to as microcrystallinity. The microcrystallinity may therefore be calculated using the following algorithm:

$$X\% = \frac{\Delta H_C - \Delta H_R}{\Delta H^*_C} * 100$$

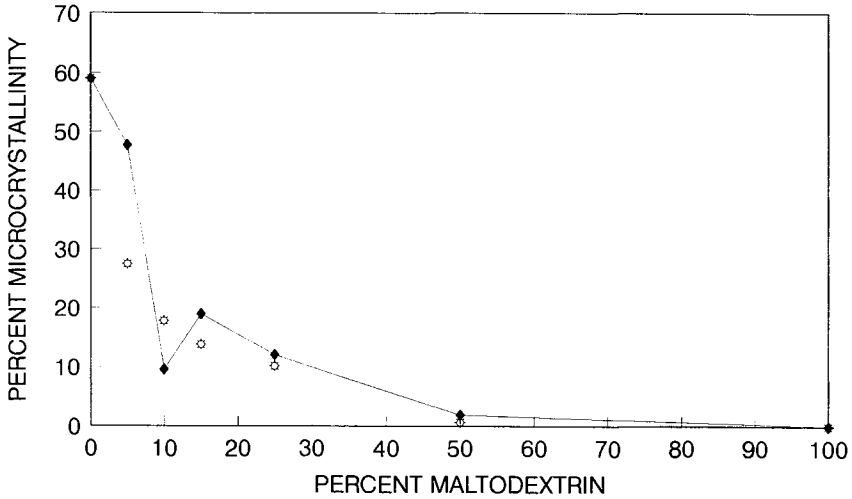

Fig. 2. Average percentage microcrystallinity vs percentage maltodextrin concentration as a function of agglomeration. (☼) Nonagglomerated; (—♦—) agglomerated.

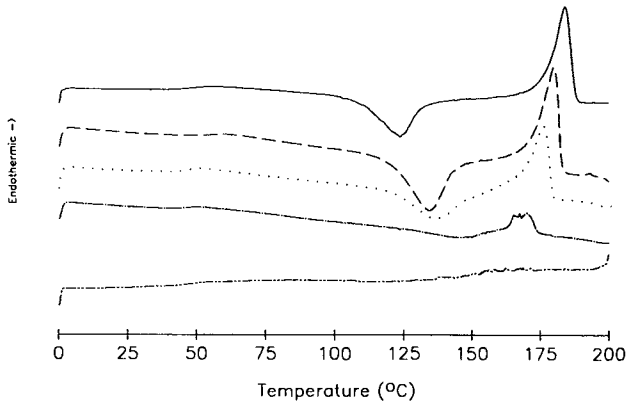

Fig. 3. Differential scanning thermograms of representative solid-state emulsions as a function of maltodextrin concentration: (——) 5%; (---) 10%; (·····) 15%; (-·-) 25%; (-···-) 50%.

where

$X\%$ = percentage microcrystallinity
ΔH_C = heat of crystallization (joules/gram)
ΔH^*_C = heat of crystallization of crystalline, anhydrous sucrose (joules/gram)
ΔH_R = heat of recrystallization (joules/gram)

The percentage microcrystallinity was calculated according to the above equation as a function of maltodextrin type and concentration (Tables I and II, nonagglomerated and agglomerated, respectively). Analysis of Table I indicates that there is essentially no difference for a given concentration between maltodextrins of different dextrose equivalents. Although samples containing M-150 (5%) and M-100 (10%) yield values higher than those for other maltodextrins at the same concentration, no clear trend is observed. Table I does indicate that there is a trend to reduce the percentage microcrystallinity as the concentration of nonagglomerated maltodextrin is increased. Similar results were observed for agglomerated maltodextrins (Table II). The compiled results for agglomerated and nonagglomerated maltodextrin are shown in Fig. 2. Analysis of Fig. 2 indicates that the microcrystallinity for the two maltodextrins decreases, in parallel, as a function of maltodextrin concentration. These results suggest that surface adsorption of oil is not the major determinant for the dispersion of oil droplets.

In addition to the decrease in the percentage of microcrystallinity, other changes brought about by the addition of maltodextrin may be observed through a direct comparison between the DSC thermogram for a sucrose-based solid-state emulsion (Fig. 1) and thermograms for maltodextrin-sucrose solid state emulsions (Fig. 3). Analysis of Figs. 1 and 3 indicates that the glass transition is increased from 38°C (100% sucrose) to 50°C (50% sucrose) as the concentration of maltodextrin is increased. Although a glass transition is always evident, the temperature of recrystallization dramatically increases at moderate concentrations of maltodextrin (15%). The recrystallization peak is essentially eliminated at and above concentrations of 50% maltodextrin. These results suggest that, with the proper amount of maltodextrin, the aging of metastable solid state emulsions can be adequately controlled.

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