

VISCOSITY AND MICROWAVE COOKING PROPERTIES OF SUGAR/MILKFAT COMPOSITES¹

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ABSTRACT

Sugar-milkfat composites with syrup consistency were prepared from sucrose, maltose or high fructose corn syrup and butteroil (20 to 40%). The components were homogenized at 40% solids and evaporated under vacuum at 60C for 60 min, leading to the formation of syrup composites with ordered structures. The viscous behavior of the syrups was described by a power law model. Flow behavior indices (0.3 to 0.9) indicated mostly pseudoplasticity, with Arrhenius-type response in consistency and flow behavior index. The sugar/butteroil composites could be microwaved to <20% moisture in approximately 60 s, producing toffee-like candies of varying color and consistency.

INTRODUCTION

Sugar based candies and pastries routinely contain large fractions of fats and sugars. The fat acts as a lubricant that increases flow and texture and improves flavor. Because of its excellent melting characteristics, milkfat is used widely in foods to enhance texture and quality. Proper and timely melting of milkfat is necessary in developing flavor and enhancing textural qualities. Cross-linking networks are formed between protein bodies and milkfat, with gelation of the mixture being facilitated by the addition of emulsifiers (Minifie 1989; Jeffery 1993).

Sugar based confectionery products such as fondants and caramels are bi-phasic composites consisting of fat and sugar components. The fat phase softens the product and intensifies flavor, while the sugar phase influences textural properties. The rheology of caramels has been described by a power law model, while the rheology of chocolate, a high fat product, is more complex, characterized by a plastic viscosity and a yield value (Chevalley 1991; Jeffery 1993; McMaster *et al.* 1988). The flow behavior of starch-fatty acid systems has been described as being dependent on triacylglycerol chain length, with the viscosity decreasing with increasing fat concentration (Raphaelides 1992); consequently, it is necessary to describe the properties and flow characteristics of sugar/milkfat composites containing large amounts of hard fat.

With microwave entrees, the issue in product formulation is lack of browning, especially with baked goods, where browning is desirable. Sugar-milkfat composites would make good browning adjuncts, provided they brown in the microwave oven. A recent development in microwave browning is the use of sugar based emulsions that brown in the microwave oven. Special mixtures of sugars, as well as honey, have been used to enhance browning and flavor (Fellenz and Moppett 1991; Rosenberg and Bogl 1987; Shukla 1994).

In this study the viscous and microwave cooking properties of sugar-milkfat (SG) composites were investigated, with the objective of developing microwaveable food grade syrups.

MATERIALS AND METHODS

Syrups were made from homogenized slurries of sugars, butteroil and emulsifiers as previously described (Onwulata and Holsinger 1996). The slurries contained 20, 30 or 40% butteroil (Land-o'-Lakes, Minneapolis, MN), and sucrose (Domino Sugar Corp, NY), maltose (Pentra Manufacturing, Livingston, NJ) or high fructose corn syrup (CornSweet™ 42, ADM Corn Processing, Decatur, IL). An emulsifying agent (mono and diacylglycerols) (American Ingredients Co., Kansas City, MO) was added at 5% of the total weight of butteroil; nonfat dry milk (Maryland and Virginia Milk Producers Association, Inc., Laurel, MD) comprised 4% of the total solids; the remainder was the selected sugar. The sugars and the nonfat dry milk were dry blended, dissolved in water, then mixed with the melted milkfat and emulsifier. The slurry was slowly brought to a final temperature of 63C and homogenized at 17.2 MPa. A syrup composite was made by evaporating the slurry at 60C under vacuum (5.2 MPa) in a rotary evaporator (Yamato Scientific Co., Tokyo, Japan). Aliquots (200 mL) were evaporated in one-liter flasks at 140 rpm for 60 min. Viscosity of each composite was measured 2 h after preparation, the composite being maintained at 20C in a water bath. Experiments were replicated 3 times.

Density was measured with an air pycnometer Model VM 100 (Horiba Instruments, Inc., Irvine, CA). Approximately 4 g samples of SG were used for each measurement; samples were replicated three times.

Moisture content of the syrups and cooked composites was determined by drying to a constant weight. The drying was done with an infra-red moisture balance (Sartorius Moisture Analyzer Ma 51, Sartorius North America, Inc., Long Island, NY) (AOAC 1984).

For evaluation of behavior when microwaved, 50 g samples of the saccharo-glyceride composites were weighed out from the 1-L flasks after rotary evaporation into Pyrex glass dishes (125 × 65 mm) and placed in a 900 Watt microwave oven (Amana Radarange, model RFS8B, Amana Refrigeration, Inc., Amana, IA). The samples were cooked until a rubbery consistency was achieved (60 s). The microwave energy was calibrated according to the IEC705 convention using 1000 mL and 350 mL water at 10 +/- 2C (George 1993). Absorbed power for three different loads of deionized water (1000, 350 and 50 mL) was 697, 683, and 266 Watts respectively. Absorbed power (Watts) is calculated from:

$$P(\text{Watts}) = (\rho V C_p \Delta T) / t \quad (1)$$

ρ = density of sample; V = volume of sample; C_p = specific heat of the material; ΔT = 10C temperature rise of sample; and t = time (s) it takes to raise the temperature of the sample load 10 +/- 2C (Padua 1993).

The Brookfield digital viscometer Model LVTDV-III attached to Rheocalc® software (Brookfield Engineering Laboratories, Inc. Stoughton, MA) was used to determine the shear response of the syrups. The small sample adapter with attached guard legs was used with spindle #3. A thermostatted water bath was used to control the temperature between 25 and 55C.

The non-Newtonian parameters for the rheological models were determined through fitting of a power law model to the data generated. Consistency and flow indices were derived from a generalized model of Herschel-Bulkley (Rao 1977):

$$\tau = \tau_0 + K \gamma^n \quad (2)$$

τ = shear stress; γ = shear rate; K = consistency index; n = flow behavior index; and τ_0 = yield stress. The yield stress was estimated from a log-log plot $(\tau)^{1/2}$ vs $(\gamma)^{1/2}$ yielding $(\tau_0)^{1/2}$ as the intercept (Rani and Bains 1987).

Tristimulus color measurements of the microwave-cooked products were evaluated instrumentally with a Gardner Model TCM infrared spectrophotometer (BYK-Gardner, Inc., Silver Spring, MD) equipped with illuminant A. Hunter L, a, and b values were obtained directly from quadruplicate measurements. The samples were rotated 90° after each measurement. Chroma (saturation index) (C) was calculated as $(a^2 + b^2)^{1/2}$. Chromaticity differences between each sample and

the standard tile were calculated as $\Delta C = (\Delta a^2 + \Delta b^2)^{1/2}$. Chromaticity differences between sample pairs were calculated as $\Delta C = [(a \text{ after microwaving} - a \text{ before microwaving})^2 + (b \text{ after microwaving} - b \text{ before microwaving})^2]^{1/2}$.

Hue angle $h^\circ = (\tan^{-1} b/a)$. The L value described the lightness of the samples directly. The reference tile reading was: L = 98.34; a = -0.21; b = 0.19. Calculations were done as described by McGuire (1992) and Little (1976).

Statistical analyses (ANOVA and Duncan's Multiple Range Test) were done with SAS for Windows™ 3.10, Version 6.08 (SAS Institute 1991).

RESULTS AND DISCUSSION

The results of evaluation of the physical properties of the SG composites are presented in Table 1. Moisture content of the composites varied despite processing under similar conditions. Time of processing was kept constant at 60 min, but composite moisture content varied significantly ($p < 0.05$) with syrup type and fat content. Product density varied significantly, but did not correlate with moisture content variation as might be expected. As moisture evaporated during the cooking process to below 20%, the components coalesced, and formed ordered structures of syrupy consistency in all cases (Onwulata and Holsinger 1996). Structure formation in confectionery products, particularly caramels, occurs during the cooking process where the breakdown of membranes and deformation of fat globules takes place. The formation of ordered structure is improved by Maillard-type reactions leading to a lowering of product viscosity at high temperatures (Xiong *et al.* 1991; Yost and Kinsella 1993; Kato *et al.* 1993). A phenomenon characteristic of high temperature boiled caramels is the lowering of the viscosity (McMaster *et al.* 1988).

Characteristic flow index and consistency values are presented in Table 2. The flow indices show that the composites followed "power-law" model equations in the range evaluated. Flow and consistency varied with increasing fat content as shown in Fig. 1 at 20C. The composites were pseudo plastic in flow behavior ($n < 1$), except for an anomaly with high fructose corn syrup at 40% fat and 40C, where the flow showed a near Newtonian behavior ($n > 1$) (Table 2). For the most part, consistency and flow (n) decreased as the temperature increased from 20 to 50C (Table 2). The sucrose/butteroil and maltose/butteroil composites were rheologically similar to the high fructose corn syrup/butteroil composite, which is used in candy manufacturing (Gingrich and Dimicki 1979). As temperature increased, the consistency "K" (Pa.s) index decreased, with consistency patterns being product dependent (Fig. 2).

Yield stress of the microwave-treated samples was affected by temperature with a general decline at temperatures of 30C and above (Table 2). There was no yield stress for the high fructose corn syrup sample with 40% fat at 40C since this

TABLE 1.
PHYSICAL PROPERTIES OF SYRUP COMPOSITES

Sample	Moisture (%)	Density (g/cm ³)	Apparent Viscosity ¹ (POISE)	Activation Energy		
				E _a	CF	R ²
CNSYRUP20	18.3/1.3	1.25/.01	14.8	63300	-16.0	0.98
CNSYRUP30	16.9/1.3	1.21/.03	33.6	33553	-3.62	0.93
CNSYRUP40	14.1/1.0	1.17/.05	71.5	79824	-22.3	0.91
MALTOSE20	17.1/1.5	1.27/.01	16.7	40254	-5.7	0.97
MALTOSE30	18.6/1.8	1.20/.03	22.2	29244	-2.0	0.99
MALTOSE40	13.9/.40	1.15/.03	7.9	42734	-8.4	0.99
SUCROSE20	15.9/1.9	1.26/.02	21.1	52266	-11.3	0.98
SUCROSE40	14.3/1.0	1.17/.02	21.5	89172	-26.0	0.88

Apparent viscosity = E_a/T-CF: CF = Correction Factor. E_a = Activation energy. T = (K).
Numbers after “/” = standard deviation. CNSYRUP20, 30, 40 = High Fructose Corn Syrup containing 20, 30 or 40% butteroil.

¹Representative sampling; mean apparent viscosity was not determined because of variation in moisture content.

anomalous sample exhibited near-Newtonian behavior. The yield stress of certain confectionery products such as molten chocolate has been reported to play a role in sensory receptivity and textural perception (Wilson *et al.* 1993). Milkfat content also affected yield stress with highest values found in samples with 30% fat, the typical fat content of most fat-containing confectionery products (Jeffery 1993).

The effect of temperature on the apparent viscosity (η^*) of the SG syrups was evaluated with a relational model:

$$\eta^* = a + \text{EXP}(b/T) \quad (3)$$

where a and b are constants; T = temperature (° Kelvin); η^* = apparent viscosity; b is the constant describing the activation energy E_a/R (kJ/mole); R = gas constant (8.3144 kJ/mole ° K). The three composites containing 20% butteroil varied highly significantly from one another (p < 0.01) at 20C but the variation was not significant at higher temperatures and fat contents. The activation energies of the flow at different fat levels are listed in Table 1. All samples showed a nonlinear

TABLE 2.
POWER LAW MODEL PARAMETERS OF SYRUP COMPOSITES

Sample	Temperature (C)	K (Pa.s)	n	Yld Stress (Apparent)	R ²
CN SYRUP20	20	4.09±.07	0.75	9.62	.999
	30	3.85±.06	0.65	11.50	.986
	40	3.47±.07	0.58	6.03	.982
	50	3.22±.09	0.66	3.13	.989
CN SYRUP30	20	3.98±.02	0.52	22.00	.997
	30	3.87±.07	0.49	19.90	.984
	40	3.53±.12	0.50	9.40	.987
	50	3.29±.09	0.45	6.84	.995
CN SYRUP40	20	4.16±.10	0.77	6.51	.988
	30	3.89±.14	0.54	13.10	.955
	40	3.09±.54	1.10	0.00	.976
	50	3.17±.16	0.79	2.38	.986
MALTOSE20	20	4.23±.38	0.82	6.49	.997
	30	3.92±.26	0.77	6.31	.989
	40	3.53±.18	0.67	4.27	.966
	50	3.36±.16	0.49	6.27	.934
MALTOSE30	20	4.09±.11	0.50	21.70	.988
	30	4.01±.08	0.51	17.20	.980
	40	3.51±.08	0.30	13.80	.979
	50	3.25±.07	0.19	10.60	.985
MALTOSE40	20	4.28±.35	0.74	6.76	.967
	30	3.96±.19	0.50	14.00	.966
	40	3.18±0.5	0.63	7.30	.983
	50	3.31±.09	0.67	3.50	.979
SUCROSE20	20	4.30±.15	0.91	4.40	.989
	30	3.95±.09	0.71	10.00	.990
	40	3.58±.02	0.70	4.78	.978
	50	3.32±.04	0.75	2.31	.991
SUCROSE30	20	4.06±.15	0.46	27.90	.994
	30	3.95±.10	0.49	23.10	.971
	40	3.61±.06	0.43	11.40	.992
	50	3.41±.08	0.45	6.80	.992
SUCROSE40	20	4.25±.14	0.73	9.00	.992
	30	3.86±.15	0.36	6.20	.939
	40	3.45±0.4	0.59	3.89	.981
	50	3.51±.01	0.50	3.87	.996

CNSYRUP20, 30, 40 = High Fructose Corn Syrup containing 20, 30 or 40% butteroil. Yld Stress: Yield Stress.

increase in flow activation energy as the ratio of sugar to fat decreased from the 40% to 20% fat mixture, passing through a minimum at 30% fat. This is in contrast to the results for high fructose corn syrup composites obtained by dynamic rheometry where activation energies were relatively stable, showing less temperature dependence (Onwulata and Holsinger 1996). Activation energies of this study, calculated from Brookfield apparent viscosity measurements, were

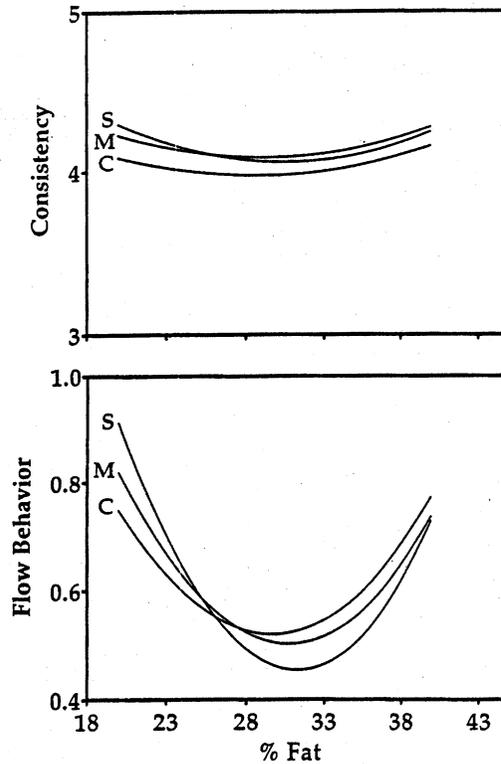


FIG. 1. FLOW BEHAVIOR AND CONSISTENCY INDICES OF SUGAR/BUTTEROIL COMPOSITES

S = sucrose; M = maltose; C = high fructose corn syrup

considerably higher than those obtained from dynamic rheometry measurements (Onwulata and Holsinger 1996). The results of this study disagree with reported increases in activation energy at higher sugar concentrations (% Brix) for fruit juices (Saravacos 1970).

Loss in flavor due to microwave cooking as expressed by the "Delta T" theory is a means of evaluating the effect of microwave heating on flavor through loss of volatile components. The ΔT is calculated as:

$$\Delta T = (T_i s - T_f s) / (T_i w - T_f w) \quad (4)$$

where T_i = Initial temperature; T_f = Final temperature; s = sample; w = water. This gives the heating rate of food samples relative to water; if the sample heats faster than water ($\Delta T > 1$) loss of flavor might result. If $\Delta T < 1$, the sample heats more slowly than water (Ramaswamy and van de Voort 1990). All the syrup composites

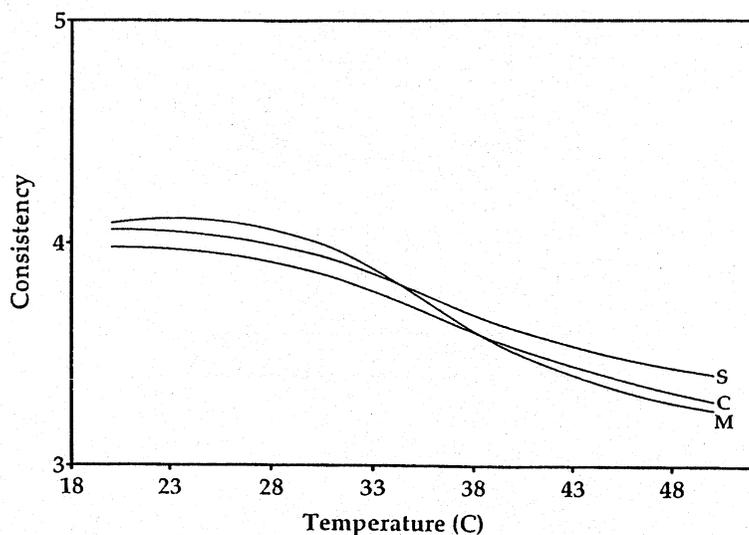


FIG. 2. CHANGE IN CONSISTENCY IN RESPONSE TO INCREASING TEMPERATURE
S = sucrose; M = maltose; C = high fructose corn syrup

had $\Delta T > 1$, which implies that composites heated faster than water and suggested flavor loss as a result (Table 3). The trend was for higher loss in flavor at high fat contents.

Highest levels of absorbed power were found in samples with 40% milkfat, corresponding to the lowest initial (Table 1) and final (Table 3) moisture contents. The moisture content of the confections after microwave cooking for 60 s varied significantly ($p < 0.05$), with the formulations containing 40% fat having consistently lower moistures (Table 3); initial moisture contents of the syrups correlated slightly ($R = .71$) to their final moisture contents after cooking. Final moisture contents of the microwaved products were within the range of those of similar confectionary products [caramels contain ~ 8% moisture (McMaster *et al.* 1988)]. The lower moisture content corresponded directly to the highest flavor loss index with each composition but absorbed energy did not correspond directly to flavor index. However, absorbed energy followed the same trend as activation energy (Table 1) with the lowest values corresponding to samples containing 30% milkfat.

Color differences in the syrups before and after microwaving, compared to the standard tile, are presented in Table 3. Differences in color ΔC varied significantly ($p < 0.05$) with sugar composition as well as with fat content. ΔC 's of maltose and high fructose corn syrup composites were not significantly different from one another but were significantly different ($p < 0.05$) from the composites containing sucrose. Color differences did not correlate with absorbed power.

TABLE 3.
PROPERTIES OF MICROWAVED SYRUP COMPOSITES

Sample	Moisture (%)	Color ΔC^1		Absorbed Power (J/s)	Flavor Index ΔT
		Pre	Post		
CN SYRUP20	8.75/0.25	1.47/0.20	5.33/4.6	403/6.8	1.75/0.3
CN SYRUP30	8.88/1.5	1.89/0.62	7.91/1.7	395/2.1	1.72/0.01
CN SYRUP40	6.67/2.6	3.13/1.4	12.47/2.8	432/15.7	1.88/0.07
MALTOSE20	8.01/2.2	2.18/1.0	10.20/4.7	367/23.5	1.51/0.05
MALTOSE30	9.48/1.5	1.04/0.18	9.36/4.3	345/12.0	1.50/0.5
MALTOSE40	7.25/1.04	3.54/2.0	9.85/3.6	405/5.8	1.76/0.03
SUCROSE20	9.81/2.6	1.23/0.09	13.70/0.7	392/9.9	1.70/0.04
SUCROSE30	9.65/1.25	1.88/0.20	12.50/1.2	367/10.7	1.60/0.05
SUCROSE40	5.89/96	3.94/0.11	13.00/0.60	415/26.8	1.81/0.12

Color¹ = Chromaticity Difference = ΔC (Differences calculated from Hunter L, a, b values of samples and those of standard tile) Pre= Color of syrup before microwave cooking. Post= Color of syrup after microwave cooking. CNSYRUP20, 30, 40 = High Fructose Corn Syrup containing 20, 30 or 40% butteroil.

Numbers after "p" = standard deviation.

A more detailed description of the effects of microwave treatment on color of the SG composites is provided in Table 4. Color analysis is extremely important when determining the effects of a particular treatment on a product. On the Hunter scale, with the instrument used, the b coordinate is a measure of yellowness. Examination of the b coordinates of the syrups before microwave treatment (Table 4) show that the three composites with 40% milkfat are more yellow than their counterparts with less milkfat; this increase is easily explained since milkfat contains significant amounts of β -carotene (Jensen 1995). All b coordinate values of sucrose-containing syrups are positive, these samples are less white and more yellow than the syrups containing high fructose corn syrup or maltose as shown by their lower lightness L values. There was little difference in color between the sample with high fructose corn syrup and 30% fat and its maltose counterpart. With high fructose corn syrup or maltose, lightness L declined with increasing amounts of milkfat, another indicator of the increase in yellowness and decrease in whiteness. Hue angle h° also decreased with increasing milkfat content in most cases, another indicator of increased yellowness as the angles approach 90° on the vertical axis of the grid. Chroma C generally increased with increasing

TABLE 4.
 COLOR CHARACTERISTICS¹ OF SYRUPS CONTAINING DIFFERENT SUGARS AND
 MILKFAT LEVELS BEFORE AND AFTER MICROWAVE TREATMENT

Sample	L	a	b	h° tan ⁻¹ b/a	C (a ² + b ²) ^{1/2}
BEFORE TREATMENT					
CNSYRUP20	49.8	-0.63	-1.21	242	1.38
CNSYRUP30	42.5	-1.27	-0.29	210	1.94
CNSYRUP40	41.2	-2.27	2.48	137	3.41
MALTOSE20	44.8	-0.98	0.07	151	2.29
MALTOSE30	42.5	-1.27	-0.36	205	1.50
MALTOSE40	40.2	-2.26	2.77	149	3.79
SUCROSE20	34.0	-1.60	0.25	171	1.63
SUCROSE30	29.1	-2.05	0.15	175	2.11
SUCROSE40	38.6	-2.87	2.90	135	4.09
AFTER TREATMENT					
CNSYRUP20	46.8	3.35	4.15	50.9	5.34
CNSYRUP30	39.5	4.26	6.59	52.4	7.92
CNSYRUP40	26.6	5.16	7.02	37.8	9.04
MALTOSE20	46.8	3.48	9.70	69.6	10.30
MALTOSE30	47.1	2.61	8.97	69.8	9.46
MALTOSE40	30.2	4.71	8.60	58.2	9.90
SUCROSE20	38.3	3.93	13.3	73.6	13.9
SUCROSE30	38.9	2.04	12.4	81.1	12.6
SUCROSE40	25.6	5.69	11.7	64.2	13.0

¹Means of three replicates per sample. L = lightness coefficient, ranging from black = 0 to white = 100; a and b = chromaticity coordinates located on a rectangular coordinate grid perpendicular to the L axis, where a = bluish-greenish/red purple hue component and b = yellow/blue hue component (on the horizontal axis, positive a = red/purple hue, negative a = bluish-green; on the vertical axis, positive b = yellow and negative b = blue) and color at grid origin (a = 0, b = 0) is achromatic (gray); h° = hue angle (0° = red/purple; 90° = yellow; 180° = bluish-green; 270° = blue); C = chroma, an index somewhat analogous to color saturation or intensity.

concentration of milkfat, again reflecting the color conferred by the milkfat. After microwave treatment, however, although all b coordinate values increased

significantly when compared to their nonmicrowaved counterparts, the yellowness decreased as milkfat content increased with the maltose and sucrose-containing syrups. Least yellow were the samples with high fructose corn syrup; hue angle h° showed that microwaved syrups containing high fructose corn syrup were more red than yellow, probably due to greater formation of Maillard compounds because of higher levels of reducing sugar. Least red after heating were syrups containing sucrose, which is not a reducing sugar. Lightness L decreased with increasing milkfat as the samples browned and darkened as a result of the microwave heating. Chroma C showed little variation with increasing milkfat content in sucrose or maltose-containing syrups but increased steadily with increasing fat content in the case of high fructose corn syrup. The numbers show that the sucrose-containing syrups have the most intense color at the point the measured coordinates describe. Visual examination after microwave heating clearly shows that sucrose samples darkened the least as a result of microwave treatment, while high fructose corn syrup solids darkened the most. These results suggest that desirable colors can be generated by microwave treatment by blending syrups to control the amount of milkfat and reducing sugar present.

Color differences between sample pairs, before and after microwaving, are shown in Table 5. Chroma difference ΔC is reported. In terms of ΔC between sample pairs, sucrose syrups showed the greatest color change as a result of microwave treatment but visually were the lightest in color after microwave treatment. Syrups with maltose showed little change in ΔC with increasing fat content as a result of microwave treatment, while samples with high fructose corn syrup showed the least difference as a result of heating, but visually were the

TABLE 5.
COLOR DIFFERENCES BETWEEN COMPOSITE PAIRS BEFORE AND AFTER
MICROWAVE TREATMENT¹

Sample	ΔC
CNSYRUP20	6.68 ^a
30	8.83 ^b
40	9.26 ^b
MALTOSE20	10.6 ^a
30	10.2 ^a
40	9.22 ^b
SUCROSE20	14.2 ^a
30	13.0 ^b
40	12.3 ^b

¹ $\Delta C = [(a_{\text{post}} - a_{\text{pre}})^2 + (b_{\text{post}} - b_{\text{pre}})^2]^{1/2}$, where post = after microwave treatment and pre = before microwave treatment.

Samples with different letters different from one another by Duncan's Multiple Range Test.
CNSYRUP20, 30, 40 = high fructose corn syrup with 20, 30 or 40% milkfat.

darkest in color. In general, while sometimes reduction of color data to a single number can be useful for describing color tolerances, information given by a single number is incomplete. The data reported in Table 4 are more useful for describing the character in each color difference for each syrup since the nature of the difference from the standard can be specified. The syrup composites responded to microwave energy by producing candies of a "toffee" consistency with an increase in the measure of color ΔC .

CONCLUSION

Sugar/milkfat composites with defined viscosity and microwave cooking properties permit their use in a variety of food processes and products. The composites mimic standard confectionery syrups made with corn syrups. Viscous properties of maltose/butteroil composites closely approximated those of high fructose corn syrup composites. Increases in milkfat resulted in browned and darkened products, making it possible to derive appropriate color through blending. Microwave cooking developed products with toffee-like consistency and browning, though with loss in flavor as predicted through a flavor loss index.

ACKNOWLEDGMENTS

The assistance of John Phillips with the experimental design is gratefully acknowledged.

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