

# Dynamic rheological and thermal characteristics of caramels

Jasim Ahmed<sup>a,\*</sup>, H.S. Ramaswamy<sup>a</sup>, P.K. Pandey<sup>b</sup>

<sup>a</sup>Department of Food Science & Agricultural Chemistry, Macdonald Campus, McGill University, Ste. Anne de Bellevue, PQ, Canada H9X 3V9

<sup>b</sup>Nellson Nutraceuticals Canada Inc., 1125, 50th Avenue, Lachine, Que., Canada H8T 3P3

Received 20 October 2004; received in revised form 31 January 2005; accepted 31 January 2005

## Abstract

Small-amplitude dynamic viscoelastic properties of three different commercial caramel formulations were studied in the range of temperature and frequencies of 20–80 °C and 0.1–10 Hz, respectively, using a controlled rate rheometer. Dynamic shear results revealed viscous behaviour for caramel samples: magnitudes of viscous modulus ( $G''$ ) were higher than those of elastic modulus ( $G'$ ), and both increased with angular frequencies ( $\omega$ ). Temperature significantly ( $P < 0.05$ ) affected both  $G'$  and  $G''$ ; however, the change was insignificant at higher temperatures and frequency. Dynamic moduli-frequency data were adequately fitted by a power law-type relationship and regression parameters did not vary with temperature. Differential scanning calorimetry (DSC) was employed to examine the thermal transition of caramels. A shift in glass transition temperature ( $T_g$ ) was noticed during thermal scanning (cooling and warming) of caramel samples. Melting and crystallization temperatures were varied among the caramels. Testing temperature and variation in compositions resulted in differences in rheological parameters, melting and crystallization temperatures of caramels. © 2005 Swiss Society of Food Science and Technology. Published by Elsevier Ltd. All rights reserved.

**Keywords:** Caramel; Dynamic rheology; Glass transition temperature; Melting point; Crystallization

## 1. Introduction

Caramel is one of the most versatile and widely used confectionery products after chocolate. Chocolate and chocolate-related confectionery account together for about 50% by volume and 60% by value of the confectionery industry globally (Bouzas, 1999). Compositionally, caramel and toffee are identical except for the difference in the moisture content of the finished products. Toffee has 3–6% moisture with darker colour, while caramel has 6–12% moisture and is lighter in colour. Properties of caramel vary depending on its intended application and are regulated by the final composition. It is incorporated in a wide range of confectionery products.

Caramel is basically a mixture of several ingredients and each ingredient has a significant role in product

formulation and characteristics. It is generally manufactured by heating a mixture of glucose syrup, milk, and vegetable fats at a temperature ranging between 118 and 130 °C (Minifie, 1989). Heating enhances the browning reaction of caramel and regulates the finished product moisture content. The Maillard reaction (non-enzymatic browning) is responsible for much of the colour and flavour development with a major reaction product formed being melanoidine plus many other compounds (deMan, 1990). The amount and type of reducing sugars controls the browning reaction, while fat-based ingredients provide the desired texture, mouth feel and shelf-life. In addition, fats have been used as a flavour carrier, stickiness reducer, for machinability assistance or stand-up quality (Bouzas, 1999). Various sugars including sucrose, corn syrup, invert sugar syrup, dextrose, and lactose have been used as carbohydrate source, while milk and/or vegetable fats have been added as fat source for providing body and texture of caramel. Recently, various dairy ingredients have been incorporated into formulations of caramels as protein

\*Corresponding author. Tel.: +1 5143988666; fax: +1 5143987977.  
E-mail addresses: jahmed2k@yahoo.com, jasim.ahmed@mcgill.ca (J. Ahmed), hosahalli.Ramaswamy@mcgill.ca (H.S. Ramaswamy), ppandey@nellsonni.com (P.K. Pandey).

source. The type and amount of protein balance the caramel formulation. Whey protein concentrates provide a cost-effective alternative to formulate caramels with good eating quality and maintain excellent process condition. In some applications, like standup caramels, a minimum amount of casein is also added to prevent cold-flow. The levels of dairy solids contribute to the emulsification and the stand-up property of the finished caramel. An optimum mixture of carbohydrates, proteins and fats in caramel products largely dictates the rheological, thermal and structural properties, and, therefore, affect the operational and functional properties (Bouzas, 1999).

Interactions of three basic ingredients namely carbohydrates, proteins and fats along with water and other minor additives during shearing, mixing and heating make an interesting combination in product formulations. Milk proteins play a major role in modifying the functional properties of caramel, while carbohydrates contribute the texture of the final stand up. Different approaches have been used to measure composition and physico-chemical properties of caramels (Chung, Ruan, Chen, & Wang, 1999; Morton et al., 2003). Among the various techniques used for structural property evaluations, rheological measurements have been considered a valuable tool to provide fundamental insights on the structural organization of food and play an important role in manufacturing process of foods like caramel where problems can arise due to the sticky nature. Caramel has a complex viscoelastic structure, but the mechanistic understanding of the viscoelastic properties of these mixtures is not well known. Small-amplitude oscillatory shear (SAOS) tests afford the measurement of dynamic rheological functions, without altering the internal network structure of materials tested (Gunasekaran & Ak, 2000), and are far more reliable and informative than steady shear measurements (Bistani & Kokini, 1983). Such detailed studies on caramel rheology helps to better characterize their structure and phase behaviour. They offer significant commercial benefits through improved product design by choosing the correct ingredients based on functionality, ensure better quality control in the final product, enhance shelf-life and stability, and promote better compatibility with manufacturing equipment. Studies on temperature effect on rheological characteristics of caramel are limited.

In recent studies, food researchers have given considerable stress on phase diagrams of food systems, which considered being systems of water plasticized natural polymers (Slade & Levine, 1991; Hartel, 2001). Materials with amorphous or partially amorphous structure undergo a transition from a glassy solid state to a rubbery viscous state at a material-specific temperature range, which is often considered as a single-point temperature for practical purposes and is called the glass transition temperature ( $T_g$ ). The transi-

tion, however, occurs over a range of temperatures rather than at a single point (Roos, Karel & Kokini, 1996; Goff, Verespej & Jermann, 2003). As the temperature increases above  $T_g$ , some of the physical properties of the material change, among them, the most important are an increase in the free molecular volume, an increase in heat capacity ( $C_p$ ), increase in thermal expansion coefficient and dielectric coefficient and changes in viscoelastic properties (Genin & Rene, 1995). Carbohydrate constituents have a major role in influencing the glass transition temperature of food systems, while the effect of protein and fat on  $T_g$  are considered minimal (Jouppila & Ross, 1994). Water works as a strong plasticizer in a food system and it decreases the  $T_g$  significantly due to its very low  $T_g$  of  $-135^\circ\text{C}$  (Johari, Hallbrucker, & Mayer, 1987; Ahmed, Ramaswamy, & Khan 2005). It has been reported that  $T_g$  has major impact on food texture/rheology (Chung et al., 1999; Hartel 2001) and food stability as the water in the concentrated serum phase becomes kinetically immobilized and hence does not support or participate in any reaction. The physico-chemical properties of foods governed by  $T_g$  are numerous including agglomeration, crystallization, structural collapse, sandiness, etc. (Rahman, 1995). Therefore, the knowledge of  $T_g$  is essential in assuring quality, stability and safety of various confectionary products (Roos et al., 1996). Crystallization (a process where the molecules in the liquid state can organize and form into crystal lattice structure under supersaturation or subcooling conditions), is an important phase of the structural elements in a wide range of food products (Hartel, 2001). The texture of different types of caramels provides an interesting example of the effect of sugar crystals on product characteristics. However, in a complex system like caramel, the influence of all other components on the phase change behaviour of the crystallizing species and crystallization kinetics must be known, and this may be a challenging task to evaluate. The crystallization kinetics are dependent on formulation as many ingredients influence nucleation and growth rate.

So far, only a limited amount of information is available on rheological and thermal properties of caramels. Therefore, the objectives of the present work were to evaluate the rheological characteristics and thermal properties (glass transition temperature, melting and crystallization) of selected commercial formulations of caramel, and examine the relationships between them.

## 2. Materials and methods

### 2.1. Materials

The major ingredients used for the caramel preparations were corn syrup, sucrose, evaporated milk, whey

protein isolate (WPI), fractionated palm kernel oil-based vegetable fat along with minor ingredients like sodium chloride, soya lecithin and xanthan gum. The corn syrups were procured from Cargill Foods, MN, fractionated palm kernel oil-based vegetable fat from AC Humko Food, Inc., Memphis, TN, WPI from Davisco, xanthan gum from CP Kelco, while others were purchased from local Montreal market.

## 2.2. Caramel preparation

The product formulations for this study are shown in Table 1. The caramel was prepared following the method described by Minifie (1989) and Chung et al. (1999). The caramels were prepared by dissolving the sucrose in water at room temperature in an electric kettle (Presto Electric Kettle model # 06003) and heated at low temperature until the sugar was dissolved. All other ingredients were added to the kettle and mixed slowly at 66 °C with continuous agitation to prevent burning and the heating continued for 10 min. Heating and mixing proceeded with the heat increase bringing the mixture to steady boiling. The temperature was finally increased to 120 °C and heating continued for 20 min for maximum caramalization. The cooking temperature was monitored by the Control Master<sup>®</sup> temperature controller (part # 06903, National Presto Industries Inc. Shelton, CT). The whole mass was mixed with continuous agitation for few minutes followed by transferring to a tray placed on a cooling table at approximately 50 °C. The samples were cooled and stored in a refrigerator before further use. The samples were semi-solid in nature at ambient condition and hard solid at refrigerated storage.

## 2.3. Dynamic rheological measurement

SAOS rheological measurements were performed using a controlled rate rheometer (AR 2000, TA Instruments, New Castle, DE) with computer control.

Table 1  
Compositions of caramels

| Ingredients (g/100 g)           | Caramel A | Caramel B | Caramel C |
|---------------------------------|-----------|-----------|-----------|
| Corn syrup                      |           |           |           |
| 43DE                            | 0         | 10        | 10        |
| 63DE                            | 25        | 28        | 28        |
| Evaporated whole milk           | 21        | 17        | 17        |
| Sucrose                         | 31        | 22        | 22        |
| WPI                             | 2.75      | 3         | 3         |
| Water                           | 11.91     | 11.66     | 11.66     |
| Sodium chloride                 | 0.9       | 0.9       | 0.9       |
| Soya lecithin                   | 0.3       | 0.3       | 0.3       |
| Butter                          | 0         | 0.5       | 3         |
| Vegetable fat (Palm kernel oil) | 7         | 6.5       | 4         |
| Xanthan                         | 0.14      | 0.14      | 0.14      |

A cone and plate geometry was used with a plate radius of 60 mm and a cone angle of 2°. The gap between the cone and plate geometry was set at 64 µm. Rheological measurements were made at temperatures ranging from 20 to 80 °C. A solvent trap was used to minimize moisture loss during the tests. The AR 2000 System was based on efficient peltier temperature control system and temperature was efficiently monitored during the experiments.

For each test, approximately 2 g caramel sample was placed between the plates. The linear viscoelastic limit for SAOS tests was determined by stress sweep tests and an applied stress of 3 Pa was selected for all experiments. Oscillatory tests were performed in a frequency range between 0.1 and 10 Hz. The instrument was programmed for set temperature and equilibrated for 10 min (relaxation step) followed by a two-cycle frequency change from 0.1 to 10 Hz and back. Temperature ramp experiments (20–80 °C) were carried out at the rate of 1 °C/min, and, at a constant frequency of 1 Hz. Each time new sample was used for rheological measurement. All rheological measurements were carried out in duplicate and the company-supplied rheology Advantage software, Version 2.3, was used to obtain property data (elastic modulus,  $G'$ , viscous modulus,  $G''$  directly) at each test frequency.

## 2.4. Differential scanning calorimetry

Thermal scanning of caramel samples were carried out using TA Q100 Differential Scanning Calorimeter (DSC) (TA Instruments, Newcastle, DE), and equipped with a refrigerated cooling system that efficiently controlled and monitored temperature up to –90 °C. The instrument was calibrated using sapphire and indium. Nitrogen was used as purge gas at a flow rate of 50 ml/min. Samples (12–15 mg) were accurately weighed into polymer-coated aluminium pans, hermitically sealed, and allowed to equilibrate at the initial temperature for 10 min. A four-axis robotic device automatically loaded the sample and reference pan of DSC. A sealed empty aluminium pan was used as a reference. Preliminary runs were used to optimize the temperature ranges of thermal scanning for glass transition, crystallization and melting temperatures.

A two-cycle process was used for all test runs of caramels. For glass transition measurement, the sample was equilibrated at –90 °C, maintained in the isothermal condition for 10 min followed by temperature scanning at 5 °C/min up to 0 °C (warming step), equilibrated at 0 °C and held for 15 min under isothermal condition and then brought back to –90 °C at 5 °C/min (cooling step). Thermal scanning was performed between 50 and –20 °C for evaluating crystallization and melting temperatures of caramels. Samples were equilibrated at 50 °C, maintained under isothermal condition for 10 min

followed by temperature ramp of 5 °C/min up to –20 °C; then equilibrated at –20 °C and maintained under isothermal condition for 15 min, and then heated to 50 °C at same ramp rate. An average value of three replicate samples was reported. Results (glass transition, melting point and crystallization temperature) were analysed using the TA Universal analysis 2000 software (Version 3.6C) (TA Instruments, Newcastle, DE). The midpoint glass transition temperature defined by the ASTM Standard (E 1356-91) (ASTM, 1995) was considered in this study, though the onset and end point  $T_g$  were also reported. The peak temperatures were taken at the maxima of the endotherms instead of the onsets, because of peak overlapping for melting ( $T_m$ ) and crystallization temperature ( $T_c$ ) (Loisel, Leco, Keller, & Ollivon, 1998).

### 2.5. Statistical analysis

Statistical analysis was carried out using Minitab statistical software package (Minitab Inc., 2000). Trends were considered significant, while means of compared sets differed at  $P < 0.05$  (student's *t*-test).

## 3. Results and discussion

### 3.1. Dynamic rheological behaviour of caramels

Dynamic viscosity parameters of caramels at 20 and 50 °C are plotted against frequency in Fig. 1. It was found that the loss modulus ( $G''$ ) was higher than the storage modulus ( $G'$ ) all through the frequency range employed, confirming the viscous nature of caramels. At frequency above 4 Hz, a destabilization process occurred that imparted to the caramel equal magnitude of both  $G'$  and  $G''$ , indicating an entangled polymer flow state. The rheological parameters  $G'$  and  $G''$  increased systematically with frequency and, the cross over of  $G'$  and  $G''$  at the higher end of the frequency range is indicative of a weaker gel. Magnitudes of both  $G'$  and  $G''$  were found to be insignificantly different ( $P > 0.05$ ) except for caramel B at the lower frequency at 20 °C; however, the difference increased significantly ( $P \leq 0.05$ ) at 50 °C for caramels B and C (Fig. 1a and b). At higher frequencies, caramels became more rigid. The increase in rigidity with frequency is probably due to the fact that some degree of relaxation is necessary for the structural rearrangement of carbohydrate and protein molecules (Kulmyrzaev & McClements, 2000). At low frequencies, the molecules have sufficient time to rearrange themselves and therefore the caramel behaves more like a fluid, while at higher frequencies, the molecules do not have sufficient time for rearrangement resulting in a more solid-like structure.

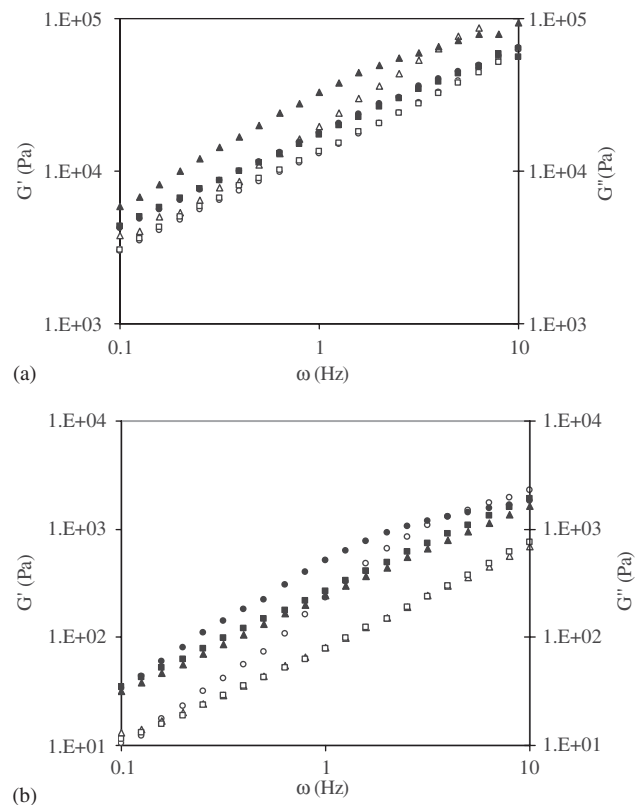


Fig. 1. Dynamic rheological behaviour of caramels at (a) 20 °C and (b) 50 °C: (○)  $G'$  of A; (●)  $G''$  of A; (△)  $G'$  of B; (▲)  $G''$  of B; (□)  $G'$  of C; (■)  $G''$  of C.

Effects of temperature (20–80 °C) on  $G'$  and  $G''$  of caramels are illustrated in Figs. 2 and 3, respectively. It is clear that both  $G'$  and  $G''$  exhibited their highest magnitude at or below 20 °C (data at 5 °C are not shown) and significantly different ( $P \leq 0.05$ ) from their values at higher temperature. At higher frequency and temperatures (40–80 °C), the values of  $G'$  were insignificantly different ( $P > 0.05$ ) except caramel A for which values at 80 °C decreased significantly (Fig. 2). A similar decreasing trend was also noticed for  $G''$ – $\omega$  curves with temperature; however, the values were more distinct compared to  $G'$ – $\omega$  curves (Fig. 3). This demonstrates that the viscoelastic properties of caramels B and C were almost similar at higher temperature and frequency, and were temperature independent. The similarities in viscoelastic properties of those caramels were attributed to similarity in their compositions except the lipid component (Table 1), while caramel A exhibited differences due to variation in dextrose equivalents of corn syrup and whey protein isolate contents.

Liquefaction of caramels at higher temperature was duly supported by Fig. 4. The semi-logarithmic plot of  $G'$  and  $G''$  against temperature at 1 Hz (Fig. 4) indicated that the viscous modulus predominated over the elastic modulus of caramels and they were temperature dependent. Interestingly, the  $G'$ – $\omega$  and  $G''$ – $\omega$  curves

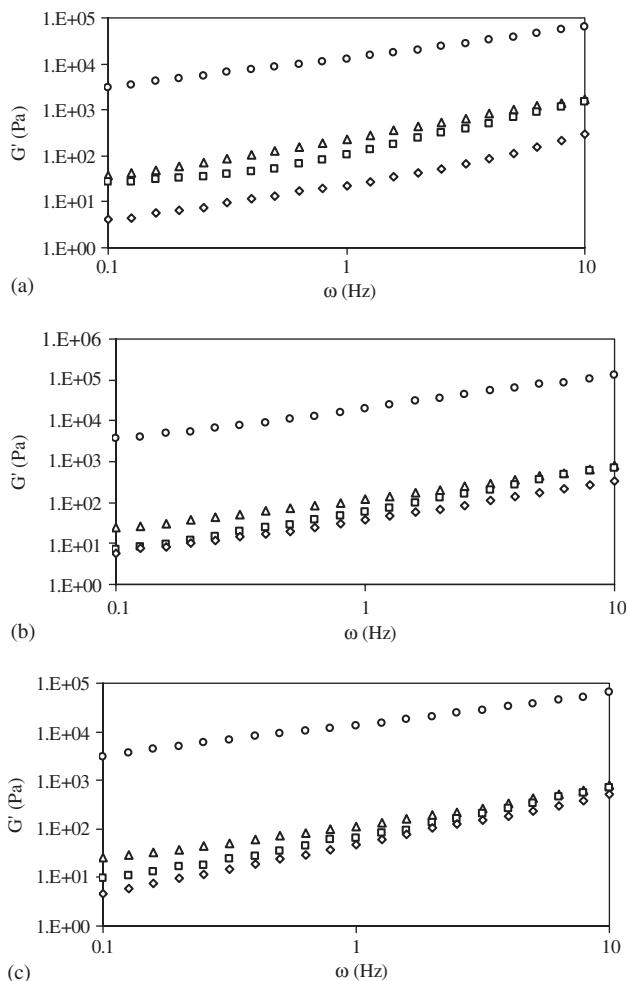


Fig. 2. Effect of temperature on storage modulus of caramels (a) A, (b) B and (c) C: (○) 20 °C; (△) 40 °C; (□) 60 °C and (◇) 80 °C.

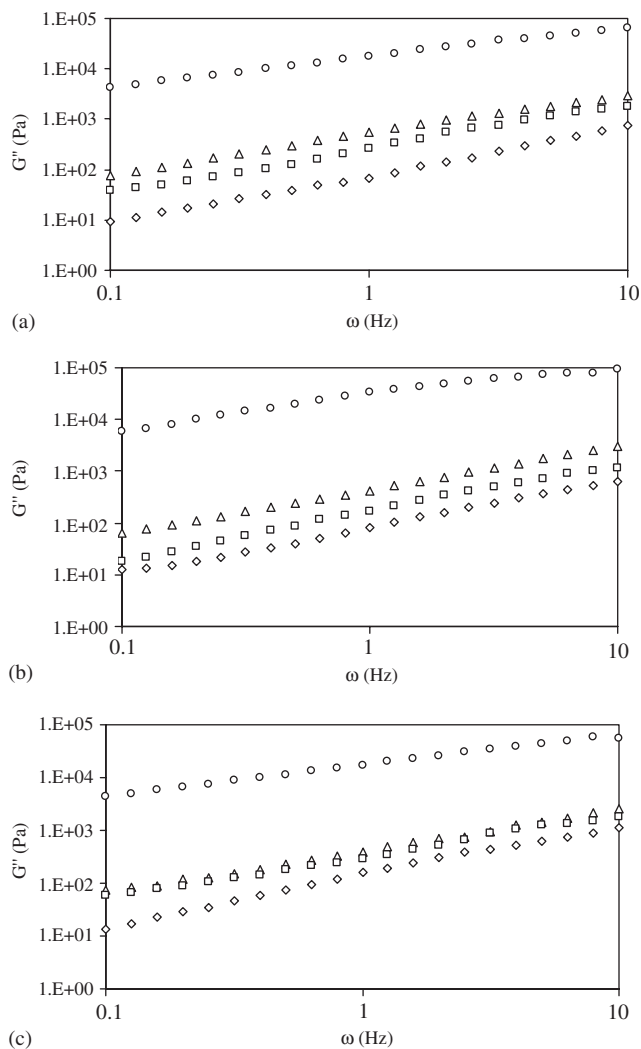


Fig. 3. Effect of temperature on loss modulus of caramels (a) A, (b) B and (c) C: (○) 20 °C; (△) 40 °C; (□) 60 °C and (◇) 80 °C.

during temperature ramp behaved differently ( $G''$  of caramels A and C were alike) as compared with the earlier observation of temperature effect on caramel. This difference in viscoelastic characteristics could be due to considerably low heating rate and thermal response of protein and sugar components in caramel matrix; however, the changes were not significant ( $P > 0.05$ ).

The dependence of  $G'$  and  $G''$  of caramels on angular frequency ( $\omega$ ) was modelled by a power-type relationship (Eq. (1)):

$$G = A\omega^b, \tag{1}$$

where  $A$  and  $b$  were empirical constants. Linear regression of  $\log \omega$  vs.  $\log G'$  and  $\log G''$  data resulted straight-line relationships (Figs. 2 and 3) and fitted adequately at all temperature ranges. The coefficients of determination ( $R^2$ ) were found to be greater than 0.97, while the standard errors were less than 0.243. The parameters of the model are listed in Table 2. A true gel is characterized by zero slope for  $\log \omega$  vs.  $\log G'$  or

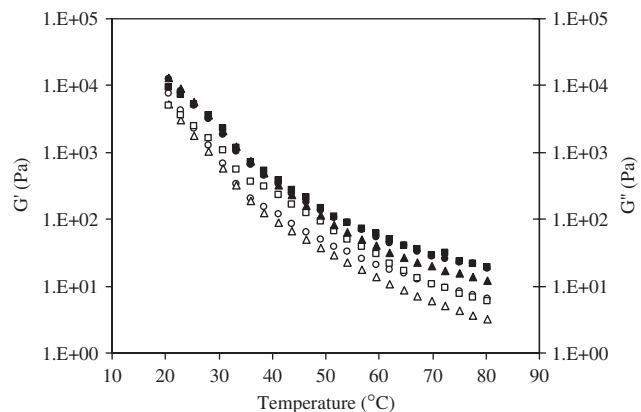


Fig. 4. Temperature dependence of the dynamic rheology of caramels at 1 Hz: (○)  $G'$  of A; (●)  $G''$  of A; (△)  $G'$  of B; (▲)  $G''$  of B; (□)  $G'$  of C; (■)  $G''$  of C.

Table 2  
Regression coefficients of Eq. (1) for caramels

| Temperature (°C)                                     | $G'$                |                          |       |       | $G''$ |                          |       |       |
|--|---------------------|--------------------------|-------|-------|-------|--------------------------|-------|-------|
|  | $b$ (dimensionless) | $A$ (Pa s <sup>n</sup> ) | $R^2$ | S.E.  | $b$   | $A$ (Pa s <sup>n</sup> ) | $R^2$ | SE    |
| (a) Regression coefficients of Eq. (1) for caramel A |                     |                          |       |       |       |                          |       |       |
| 20   | 0.655               | 13477                    | 0.999 | 0.029 | 0.600 | 20252                    | 0.999 | 0.033 |
| 40   | 0.860               | 239                      | 0.998 | 0.043 | 0.801 | 126                      | 0.998 | 0.054 |
| 50   | 0.864               | 188                      | 0.994 | 0.091 | 0.867 | 85                       | 0.969 | 0.229 |
| 60   | 0.919               | 135                      | 0.970 | 0.233 | 0.900 | 64                       | 0.996 | 0.078 |
| 70   | 1.164               | 46                       | 0.985 | 0.202 | 1.084 | 46                       | 0.999 | 0.057 |
| 80   | 0.934               | 26                       | 0.993 | 0.114 | 0.950 | 41                       | 0.997 | 0.064 |
| (b) Regression coefficients of Eq. (1) for caramel B |                     |                          |       |       |       |                          |       |       |
| 20   | 0.798               | 13684                    | 0.997 | 0.060 | 0.610 | 17309                    | 0.979 | 0.130 |
| 40   | 0.764               | 121                      | 0.998 | 0.048 | 0.849 | 514                      | 0.999 | 0.011 |
| 50   | 0.888               | 104                      | 0.998 | 0.059 | −.870 | 388                      | 0.999 | 0.032 |
| 60   | 1.027               | 131                      | 0.997 | 0.077 | 0.926 | 260                      | 0.997 | 0.070 |
| 70   | 1.023               | 59                       | 0.996 | 0.082 | 0.984 | 127                      | 0.997 | 0.074 |
| 80   | 0.865               | 48                       | 0.991 | 0.112 | 0.907 | 81                       | 0.996 | 0.078 |
| (c) Regression coefficients of Eq. (1) for caramel C |                     |                          |       |       |       |                          |       |       |
| 20   | 0.636               | 28302                    | 0.999 | 0.024 | 0.580 | 17001                    | 0.997 | 0.039 |
| 40   | 0.731               | 434                      | 0.996 | 0.060 | 0.817 | 371                      | 0.999 | 0.040 |
| 50   | 0.775               | 236                      | 0.990 | 0.109 | 0.875 | 266                      | 0.999 | 0.020 |
| 60   | 0.985               | 164                      | 0.972 | 0.243 | 0.846 | 400                      | 0.998 | 0.050 |
| 70   | 1.020               | 111                      | 0.998 | 0.057 | 0.926 | 187                      | 0.997 | 0.068 |
| 80   | 1.014               | 82                       | 0.999 | 0.025 | 0.968 | 140                      | 0.995 | 0.093 |

$\log G''$  (Ross-Murphy, 1984), while weak gels and concentrated solution/dispersions will have positive slopes. In the present study, the slopes ( $b$ ) were positive and increased with temperature resulting in a decrease in solid-gel characteristics, while the intercept ( $A$ ) decreased in a manner similar to shear thinning in flow model. The results indicated that structural changes took place during thermal treatment of caramels and they behaved like liquid at elevated temperatures. A significant change in the rheological parameters between 20 and 40 °C was contributed by the melting nature of the caramels (discussed later).

### 3.2. Glass transition temperatures

The glass transition temperatures were determined from the heat flow thermograms of DSC. The thermograms were very repeatable with different replications. The average standard error of the mean for temperatures in the total heat flow curves was 0.11, while it was 0.13 °C during reversing heat flow curves. Fig. 5 shows a typical DSC scanning curves for glass transition measurements of caramels during warming up. The glass transition is a region that includes a step change in heat capacity/heat flow in the thermogram. Clear glass transitions were observed during both warming and cooling on heat flow signal and were characterized by three points of glass transition (onset, midpoint and end temperatures) using the manufacturer-supplied soft-

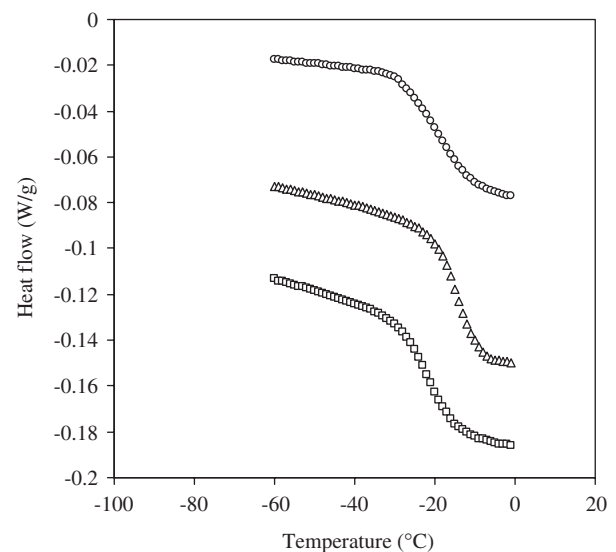


Fig. 5. Thermal transitions of caramels A, B and C during warming step: (○) A; (△) B; and (□) C.

ware. The three temperatures of  $T_g$  for each type of caramel during warming and cooling are provided in the Table 3.  $T_g$  varied between  $-13.7$  and  $-27.8$  °C. Differences were observed in the magnitudes of  $T_g$  between warming and cooling runs with  $T_g$  achieved during warming always lower than that achieved in the cooling test for all the samples. During studies on glass

Table 3  
Glass transition temperatures of caramels during cooling and warming in the total heat flow curve

| Caramel type and step | Onset (°C) | Midpoint (°C) | End (°C) |
|-----------------------|------------|---------------|----------|
| A, Warming            | −27.79     | −19.23        | −12.47   |
| A, Cooling            | −19.33     | −26.79        | −38.57   |
| B, Warming            | −15.92     | −14.46        | −10.79   |
| B, Cooling            | −13.68     | −19.27        | −30.78   |
| C, Warming            | −27.27     | −22.06        | −15.44   |
| C, Cooling            | −19.96     | −28.33        | −38.10   |

Onset and end represent the lowest and highest temperature values, respectively.

transition of caramels using dynamic mechanical analysis (DMA) and nuclear magnetic resonance (NMR), Chung et al. (1999) reported that the  $T_g$  range from  $-12.3$  to  $-26.3$  °C. Mizuno, Mitsuiki, and Motoki (1999) reported that the  $T_g$  for the same material may differ slightly or significantly, depending on the definition, the experimental conditions (heating/cooling rate) and the technique used. However, variations of  $T_g$  (during warming and cooling) in the present situation could be related to structural phenomenon at subzero temperature and the behaviour of crystals of individual compositions during warming and cooling. Goff et al. (2003) observed differences in  $T_g$  for frozen sucrose solutions using cryo-scanning electron microscopy and they advocated that the structure on the first cooling step was developed by quiescent freezing—deep under cooling followed by rapid nucleation. During warming, the structure resulting from freezing regime, most but not all of the crystals, were melted, while in the next cooling step the remaining crystals (with no further nucleation) were allowed to grow and to accelerate recrystallization. Inclusion of sugar in the crystal could thus be another reason for difference in  $T_g$  during the two steps.

Among the three caramels, lowest  $T_g$  was observed for C, while caramel B had the maximum. The observed difference in  $T_g$  among caramels may be explained on the basis of interaction among the ingredients during preparation. In addition, inclusion of sugar molecules (two different DE of corn syrup and sucrose) could influence ice crystals during freezing and play a major role contributing to variation in glass transition temperatures (Goff et al., 2003).

The melting curves obtained during DSC scanning of caramels are presented in Fig. 6. The melting point recorded as the transition at the peak, using the software, was found to vary among three caramel samples. The melting of caramel A initiated at  $23.4$  °C ( $-0.153$  W/g), while the peak melting temperature was recorded at  $31.2$  °C ( $-0.259$  W/g). The corresponding initial and peak temperatures for B and C were found to

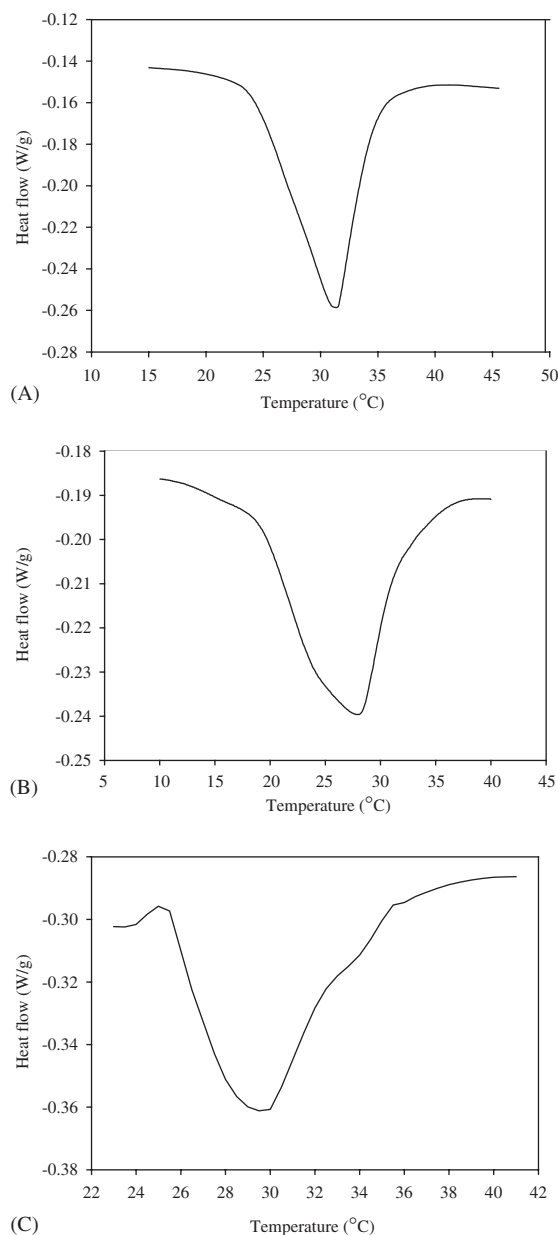


Fig. 6. Melting points of caramels A, B and C.

be  $19.4$  °C ( $-0.198$  W/g),  $26.6$  °C ( $-0.234$  W/g) and  $18.8$  °C ( $-0.232$  W/g),  $27.3$  °C ( $-0.294$  W/g), respectively. The melting behaviour of caramels was mainly controlled by the nature of fats used in the formulation. The sharp melting point peak of caramel A could be attributed to the fractionated palm kernel oil-based fat (melting point =  $32.25$  °C) used in its formulation, while in B and C some added milk fat (melting point =  $28$ – $35$  °C) contributed to a mixed behavior.

Representative DSC cooling scans for evaluating the crystallization temperatures of caramels are shown in Fig. 7. All three caramels exhibit a broad endothermic peak with an onset and a peak temperature. The crystal

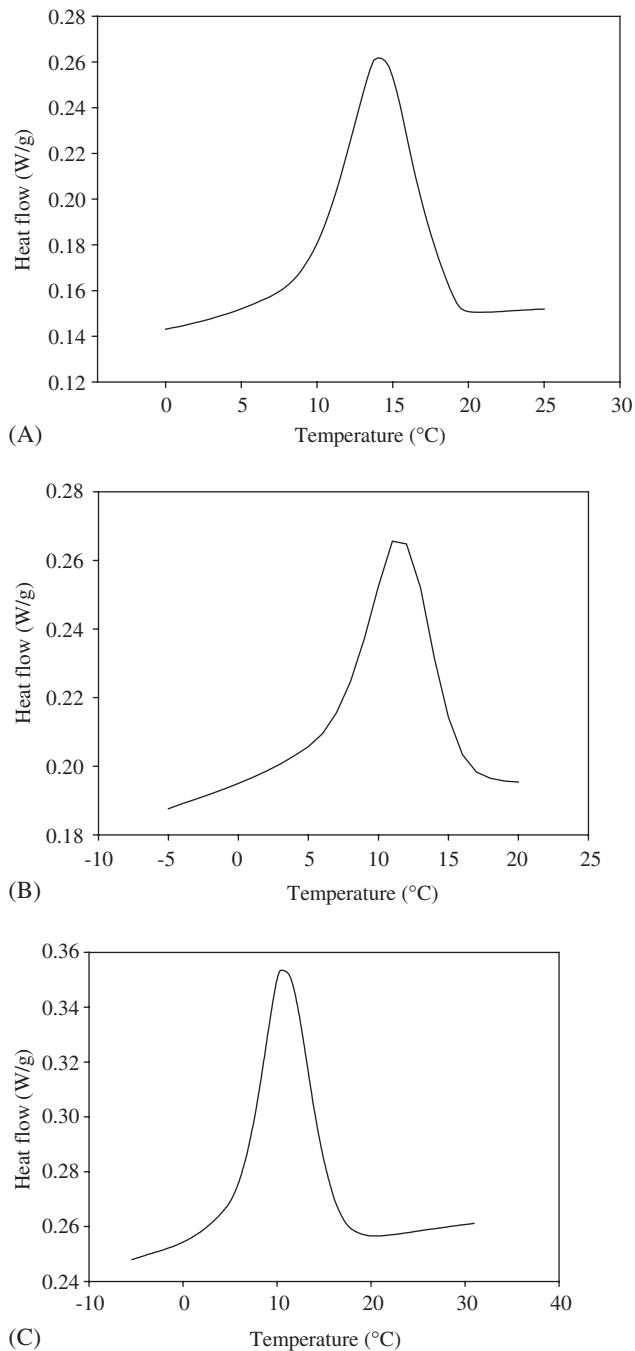


Fig. 7. Crystallization temperature of caramels A, B and C.

formation initiated at 19.4 °C (0.153 W/g), while the peak crystallization temperature was found at 14.2 °C (0.262 W/g) for caramel A. The corresponding initial and peak temperatures for B and C were observed at 16.5 °C (0.200 W/g), 11.3 °C (0.266 W/g) and 19.4 °C (0.228 W/g), 16.1 °C (0.304 W/g), respectively. Again, the differences of crystallization temperatures were due to the ratio of sucrose to corn syrup (corn syrup is

expected to depress the solubility of sucrose) and the nature of fat. The presence of corn syrup also affects the nucleation and growth rate kinetics, and thus may influence the relative shapes of the crystallization curves (Hartel, 2001).

#### 4. Conclusion

Dynamic rheological and thermal properties of three different formulations of caramel were studied. Small-amplitude oscillation measurement of caramel samples revealed that viscous modulus predominated over elastic component, and the caramels behaved like liquid at higher temperature. A shift of  $T_g$  was found during warming and cooling for all the caramel samples. This could have resulted from the nature of sugars, dextrose equivalent, inclusion of sugars in ice crystals and disorder of crystals. The variation in melting and crystallization temperatures was attributed to the fat component of caramel formulations.

#### References

- Ahmed, J., Ramaswamy, H. S., & Khan, A. R. (2005). Effect of water activity on glass transition of date paste. *Journal of Food Engineering*, *66*, 253–258.
- ASTM. (1995). *E-1356-91 Standard test method for glass transition temperatures by differential scanning calorimetry or differential thermal analysis*. West Conshohocken, PA: American Society for Testing and Materials.
- Bistani, K. L., & Kokini, J. L. (1983). Comparisons of steady shear rheological properties and small amplitude dynamic viscoelastic properties of fluid food materials. *Journal of Texture Studies*, *14*, 113–124.
- Bouzas, J. (1999). Whey products and lactose in confectionery applications. *Application Monograph* (pp. 2–8). US Dairy Export Council.
- Chung, M. S., Ruan, R. R., Chen, P. L., & Wang, X. (1999). Physical and chemical properties of caramel systems. *Lebensmittel-Wissenschaft und-Technologie*, *32*, 162–166.
- DeMan, J. M. (1990). *Principles of Food Chemistry*. NY, USA: Avi Publication pp.100–112.
- Genin, N., & Rene, F. (1995). Analyse du role de la transition vitreuse dans les procedes de conservation agro-alimentaire. *Journal of Food Engineering*, *26*, 391–407.
- Goff, H. D., Verespej, E., & Jermann, D. (2003). Glass transitions in frozen sucrose solutions are influenced by solute inclusions within ice crystals. *Thermochimica Acta*, *399*, 43–55.
- Gunasekaran, S., & Ak, M. M. (2000). Dynamic oscillatory shear testing of foods—selected applications. *Trends in Food Science and Technology*, *11*, 115–127.
- Hartel, R. W. (2001). *Crystallization in Foods*. Maryland, USA: Aspen Publishers, Inc pp. 1–9.
- Johari, G. P., Hallbrucker, A., & Mayer, E. (1987). The glass liquid transition of hyperquenched water. *Nature*, *330*, 552–553.
- Jouppila, K., & Ross, Y. H. (1994). Glass transition and crystallization of milk powders. *Journal of Dairy Science*, *77*(7), 1799–1807.
- Kulmyrzaev, & McClements, D. J. (2000). High frequency shear rheometry of honey. *Journal of Food Engineering*, *45*, 219–224.



- Loisel, C., Leco, G., Keller, G., & Ollivon, M. (1998). Dynamic crystallization of dark chocolate as affected by temperature and lipid additives. *Journal of Food Science*, *63*, 73–79.
- Minifie, B. W. (1989). *Chocolate, cocoa, and confectionery: science and technology* (3rd ed). NY: AVI 904pp.
- Mizuno, A., Mitsuiki, M., & Motoki, M. (1999). Glass transition temperature of casein as affected by transglutaminase. *Journal of Food Science*, *64*, 796–799.
- Morton, D. N., Roberts, C. J., Hey, M. J., Mitchell, J. R., Hipkiss, J., & Vercauteren, J. (2003). Surface characterization of caramel at the micrometer scale. *Journal of Food Science*, *68*, 1411–1415.
- Rahman, M. S. (1995). *Food properties hand book*. Florida: CRC pp. 118–145.
- Roos, Y. H., Karel, M., & Kokini, J. L. (1996). Glass transition in low moisture and frozen foods; effect on shelf life and quality. *Food Technology*, *50*, 95–108.
- Ross-Murphy, S. B. (1984). Rheological methods. In H. W. S. Chan (Ed.), *Biophysical methods in food research* (p. 102). London: Blackwell Scientific Publications.
- Slade, L., & Levine, H. (1991). Beyond water activity: Recent advances based on an alternative approach to the assessment of food quality and safety. *Critical Reviews in Food Science and Nutrition*, *30*, 115–360.