Correlation of low field nuclear magnetic resonance relaxation with composition and glass transition of hard candies

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Hard candies produced from sucrose and doctoring agents such as glucose syrup (GS) and high fructose corn syrup (FS) have been investigated in terms of their final composition, glass transition temperature (T_g), degree of crystallinity, total soluble solids (TSS) content and water activity (a_w). Time domain (TD) ^{1}H NMR longitudinal relaxation time (T_1) and second moment (M_2) measurements have been used to understand the glassy state and crystallization characteristics for different hard candy formulations. The investigated candies include sucrose as the main sugar component. Different levels of doctoring agents have been mixed with sucrose to obtain products with different characteristics. It has been shown that addition of any doctoring agent to sucrose formulations decreases the T_g of the system significantly ($p \leq 0.05$). Furthermore, GS or FS addition also induce significant changes in TSS and a_w. T_1 and M_2 results are almost parallel to each other, both reaching the highest values for the highest sucrose concentration ($p \leq 0.05$). The results demonstrate that the glass transition and crystallization characteristics of hard candy formulations can be monitored and analyzed by TD NMR relaxometry, alternative to other frequently used conventional methods including differential scanning calorimetry (DSC) and X-ray diffraction.

KEYWORDS

1 H NMR, hard candy, glass transition, crystallization, sucrose

1 Introduction

Hard candies are glassy confections prepared usually by mixing sweeteners such as sucrose and doctoring agents, mostly corn syrup (Lans et al., 2018). After mixing the components in the presence of additional water, the mixture is heated up to elevated temperatures for concentrating and then cooled down below T_g to reach the glassy state which provides some kinetic constraints (Hartel et al., 2011). T_g is an important parameter which determines the physical properties of hard candies. Below T_g, the amorphous solid portion of the semi-crystalline sample is defined as glassy state. This amorphous solid portion can also be transformed into a rubbery state above T_g (Tan and Kerr, 2017). In the glassy state, the molecular mobility is restricted and the product is considered stable at least for some time interval. However, glassy state is not a thermodynamically stable but a pseudo kinetically stable state (Sherwin and Labuza, 2006). Therefore, slow changes such as crystallization of sucrose can still take place in the hard candies even below their T_g

making the control of the environmental conditions a necessity (Schugmann and Foerst, 2022). Nevertheless, controlling the environmental conditions such as relative humidity (RH) and temperature is not always easy. Thus, changes in the candy formulation can also be considered to produce more stable products especially to storage conditions. For this purpose, doctoring agents including corn syrups could be used in candy formulations (Lans et al., 2018). Such agents have substantial amounts of simple sugars that can incorporate between the sucrose molecules and interfere with the crystal lattice formation by sucrose molecules (McFetridge et al., 2004). In addition to simple sugars, higher MW sugars may also be present in doctoring agents to some extent and they may contribute to the restriction of the molecular mobility by increasing the viscosity of the system (Raudonus et al., 2000). Under such conditions, incorporation of sucrose molecules thus, crystallization within the hard candies becomes harder.

The physicochemical changes taking place in the glassy state of hard candies during storage are mostly undesirable since the resulting product would be unacceptable in terms of sensorial and textural properties (Hartel, 2002). Water migration and temperature difference are the two main reasons for hard candy deterioration during storage. If the RH of the surrounding air is higher than the water activity (a_w) of the hard candy, the sample absorbs moisture (Torres et al., 2011). Water acts as a plasticizer and decreases the T_g below the storage temperature resulting in increased molecular mobility in the system (Roos, 2002). Depending on the candy characteristics, samples may become sticky or experience graining (sucrose crystallization) (Nowakowski and Hartel, 2002). If the candy formulation includes large amounts of glucose and fructose, the hygroscopic character of such sugars may induce extreme water absorption and a sticky product (Dinesh Kumar et al., 2021). In the case of high sucrose concentrations, lower levels of moisture may be absorbed by the product but the water in the candy would have higher mobility in the absence or low level of humectants. Consequently, sucrose would be able to use the free water to recrystallize. In such products, generally, graining is initially observed on the surface and crystallization continues into the interiors as the time passed (Netramai et al., 2018). These hard candies may not show stickiness but exert extreme graining lowering the sensorial and textural attributes. Therefore, a trade-off should be made between the stickiness and graining properties by controlling the storage conditions and more importantly hard candy formulations (Lans et al., 2018).

Doctoring agents also prevent or retard sucrose crystallization during the cooling period of the hard candy production primarily by increasing the viscosity of the system (Netramai et al., 2018). Additionally, GS and FS contain considerable amount of glucose and fructose in total. These sugars can both decrease the level of crystallization and increase the sweetness of the sample. They also act as humectants and reduce the risk of graining during storage (Nadaletti et al., 2011). Maltose is also present in GS and FS. It is also a relatively soluble sugar which is able to increase the system viscosity, retarding the crystallization process. The same effect can also be provided by the higher MW oligosaccharides present especially in GS (Ihli and Paterson, 2015).

The most critical phase in the hard candy production is the glass transition process. At T_g, products experience changes in various physicochemical and mechanical properties including viscosity, molecular mobility, specific heat capacity (c_p), dielectric constant and hardness (Ergun et al., 2010). Understanding the glass transition process is critical since the main purpose of the cooling of boiled hard candy mixtures is to reach a widely frozen-in thermodynamic non-equilibrium glassy state in which most of the physicochemical changes are restricted (Roos, 2002). The glassy state must be provided for each candy formulation otherwise; the end of shelf life of the products would be unacceptably close (Ergun et al., 2010). One classical method for observing the glass transition process and detecting T_g is DSC. Despite its ability to detect T_g, DSC cannot be used to observe the degree of crystallinity and the crystal content of the glassy products due to the thermal decomposition of the confections before the melting point (Lee et al., 2011). The X-ray diffraction technique is also used for crystallinity measurements, but the biased interpretation of the peaks may induce errors in the obtained results. Furthermore, mixed systems such as hard candies may produce merged peaks that are difficult to distinguish from each other (Le Botlan et al., 1998). Fourier-transform Infrared Spectroscopy (FTIR) can also be considered for crystal content measurements but its limited range of applicability to moisture prevents the analysis of some samples (Nunes et al., 2005). Another alternative is microscopy but the sample should be transparent and have low density matrix which is not suitable for hard candy samples (Martins et al., 2005).

TD NMR, on the other hand, can estimate the crystal content and degree of crystallinity in a simple and fast manner (Hashemi et al., 2010). TD NMR is also frequently used as an official method for solid fat content (SFC) measurements (Teles Dos Santos et al., 2014). The free induction decay (FID) acquired after a single pulse and the subsequent proton relaxation data are used to distinguish solid and liquid fractions of a material (Günther, 2013). However, just applying FID results in loss of signal acquired by the solid fraction due to the 'dead time' phenomenon which is caused by the delay in the record of the signal by the receiver (Dejong and Hartel, 2016). Solids relax faster than liquids due to the closer proximity of the atoms in solid materials and some proportion of this initial signal cannot be detected by the hardware leading to erroneous solid to liquid fraction calculations (Grunin et al., 2019). In order to overcome this problem, some correction factors have been previously implemented but the requirement of calibration due to the moisture sensitivity of such factors limits the use of this approach (Kovrlija and Rondeau-Mouro, 2017). Alternatively, Magic Sandwich Echo (MSE) sequence (a modified solid echo (SE) sequence) has previously been implemented to exclude the 'dead time' problem since MSE provides refocusing during the relaxation decay. This method enables the detection of the larger part of the signal coming from the solid (crystalline) fraction and eliminates the multiparameter fitting of the 'bead' pattern FID signal. In this way, second moment (M_2) can be calculated solely by the direct integration of the fast Fourier-transform of the MSE signal (Grunin et al., 2019). In addition to M_2 measurements for the detection of degree of crystallinity of hard candies, longitudinal relaxation time (T_1) can also be used to for the same purpose. T_1 is

TABLE 1 Initial sugar and syrup contents of sample mixtures (hard candy formulations).

Proportion (%)			
Sample	Glucose Syrup	Fructose Syrup	Sucrose
100:0_FS	-	100	0
75:25_FS	-	75	25
50:50_FS	-	50	50
25:75_FS	-	25	75
100_S	-	-	100
25:75_GS	25	-	75
50:50_GS	50	-	50
75:25_GS	75	-	25
100:0_GS	100	-	0

calculated by applying inversion recovery (IR) or saturation recovery (SR) sequences and a subsequent relaxation spectrum analysis (Hashemi et al., 2010). Le Botlan et al. (1998) have used T_1 to detect and quantify the crystallinity of different sugars.

In this study, we have analyzed the glass transition and crystallinity characteristics of different hard candy formulations. In addition to the final composition, T_g, TSS and a_w calculations, TD NMR measurements have been performed to understand the physicochemical properties of the samples at glassy state. The addition of doctoring agents (GS and FS) to sucrose hard candies at different concentrations had substantial impacts on almost all parameters analyzed. The use of MSE sequence provided the acquisition of all solid signal from the sample and enabled us to monitor the degree of crystallinity of hard candy samples right after the production. TD NMR results showed that crystallinity of the hard candy formulations can be detected and analyzed by M_2 and T_1 measurements.

2 Materials and methods

2.1 Samples

In order to prepare hard candy samples; sucrose (Balküpü, Turkey), high fructose corn syrup (FS) (SMF 42 Sunar Glukoz Fruktoz Surubu, Sunar Mısır, Turkey), glucose syrup (GS) (SCG 60 Glukoz Şurubu, DE 57–64, Sunar Mısır, Turkey), and water were used. Syrups and sucrose were mixed up with the proportions indicated in Table 1. Additionally, 5 mL water was added to each 50 g sugar mixture in order to form a solution. Then, all samples were boiled up to 130°C in 140°C oil bath. Only 100% (w/w) sucrose candy (100_S) could not be heated up to 130°C due to crystallization; therefore, it was terminated when 121°C was reached. After reaching 130°C, samples were poured into molds then kept for cooling down to room temperature. Temperatures of the samples were constantly monitored in the oil bath. After cooling, samples were stored in sealed pans. Each sample was made three times for the respective measurements.
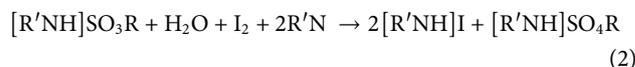
2.2 Sugar profile of syrups by high performance liquid chromatography

Syrup samples were weighed 1 g, and then mixed with 50 mL high performance liquid chromatography (HPLC) grade water (Milli-Q Water System, Millipore S.A., France) according to the procedure previously described in the reference study (Namlı, 2019). Then to hydrate completely, mixtures were stirred by vortex shaker for 5 min. After shaking, with 0.45 μm nylon filter, the solutions were filtered and introduced to HPLC vials. For the analysis, HPLC-RID (Shimadzu Scientific Instruments, Japan) instrument with auto-sampler (SIL-20A HT), degasser (DGU-20A₅), pump (LC-20AD), column oven (CTO-20A) and refractive index detector (RID-20A) were used. As the column, the inertsil NH_2 column (Shimadzu Scientific Instruments, Japan) (dimensions of 250 × 4.6, 5 μm) was used. Acetonitrile and water (80:20 v/v) mixture was used as the mobile phase during the chromatographical separation.

2.3 Water properties of hard candy formulations

2.3.1 Water content

Due to the low water content of hard candies, Karl-Fischer (KF) titration method was used for determination of water content (Fischer, 1935). The reaction occuring during titration is described by Equations 1, 2 as follows:

$$R - OH + SO_2 + R'N \rightarrow [R'NH]SO_3R + H_2O + I_2 + 2R'N \quad (1)$$
$$[R'NH]SO_3R + H_2O + I_2 + 2R'N \rightarrow 2[R'NH]I + [R'NH]SO_4R \quad (2)$$

By the help of the electrical potential difference occurred in between I_2/I^- couple, the water content can be estimated stoichiometrically. As water that is in the titration chamber depletes, electrical potential gradient goes to a constant value. When the rate of change drops under the threshold determined as 50 μS, the reaction is ended, and water amount is calculated. The analysis was made by Karl Fischer Titrator (TitraLab KF1000 Series, HACH, UK) at 25°C with a 2 component system with three replicates.

2.3.2 Water activity

In addition to water content determination, a_w of the samples were measured by using water activity analyzer (LabStart–a_w, Novasina, Switzerland). The principle of the measurement is based on the equilibrium relative humidity (ERH) method (Subranamiam and Wareing, 2016).

2.4 Total soluble solids (TSS)

TSS values of the hard candies were measured by the refractive index method (HI 96801 Refractometer, HANNA Instruments, United States) (Yebra-Biurrun, 2005). Hard candy samples were melted first and then their TSS values were measured. Since hard candy melts are highly viscous materials, the moisture loss during melting was neglected.

TABLE 2 Glass transition temperatures and specific heat capacity changes at glass transition of each component in the hard candy formulations.

Component	Δc_{pi} (J/g °C)	T_{gi} (°C)
Water	1.94 (Sugisaki et al., 1968)	−135 (Johari et al., 1987)
Fructose	0.75 (Roos, 1993)	5 (Ergun et al., 2010)
Glucose	0.63 (Roos, 1993)	31 (Ergun et al., 2010)
Maltose	0.61 (Roos, 1993)	87 (Ergun et al., 2010)
Sucrose	0.60 (Roos, 1993)	66 (Ergun et al., 2010)
DP_3	0.47 (Roos and Karel, 1991a)	112 (Avaltroni et al., 2004)
DP_n	0.40 (Roos and Karel, 1991b)	180 (Avaltroni et al., 2004)

[1]DP_3 and DP_n, represent oligosaccharides with three and more sugar molecules, respectively.

2.5 Calculation of glass transition temperature

T_g values of the samples were calculated by using an empirical expression which reflects the compositional dependence. Normally, the Gordon–Taylor equation is used for the calculation of the T_g of binary mixtures (water and a single solute) (Gordon and Taylor, 1952). This equation shows the plasticizing effect of water on T_g. However, the Gordon–Taylor equation is not suitable for the current multicomponent systems like the ones used in this study. Therefore, a modification of the equation for the T_g calculation of polymer mixtures could be considered for the multicomponent hard candy systems. This equation provides a good fit to the experimental data at high sugar concentrations (>70% w/w). Since the hard candy samples used in this study has even higher sugar concentrations, the following Couchman–Karasz expansion equation (Eq. 3) was used for T_g calculations (Couchman and Karasz, 1978; Mayhew et al., 2017):

$$T_g = \frac{\sum_{i=1}^{n} w_i \Delta c_{pi} T_{gi}}{\sum_{i=1}^{n} w_i \Delta c_{pi}} \qquad (3)$$

where w_i, Δc_{pi} and T_{gi} denote the mass fraction, change in the specific heat capacity at the glass transition and glass transition temperature of each component in the mixture, respectively. Table 2 summarizes the Δc_{pi} and T_{gi} values of each component in the hard candy formulations.

2.6 Time domain nuclear magnetic resonance relaxometry

For the TD-NMR experiments, 0.5 T (20.34 MHz) low resolution NMR System (Spin Track, Resonance Systems GmbH, Kirchheim/Teck, Germany) having 10 mm radiofrequency (RF) coil was used. Mono- and multi-exponential fittings of the relaxation spectra and the calculation of the spectral line M_2 values were performed by the Relax8 software package (Resonance Systems GmBH, Kirchheim, Germany).

2.6.1 Longitudinal relaxation time

An SR sequence having a relaxation period of 10 s and a delay time between 5–1,500 ms for 16 points was used with 4 scans to measure T_1.

FIGURE 1
Representation of an MSE sequence.
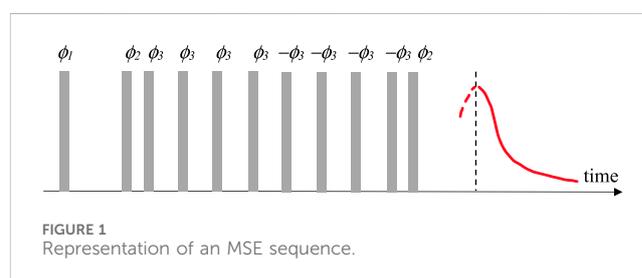
2.6.2 Second moment

M_2 values were obtained by MSE sequence (see Figure 1) having 10 s repetition delay and 4 scans per each step of the cycling of phases ϕ_1, ϕ_2 and ϕ_3 as described in a previous study (Grunin et al., 2019). The number of points that were used for FID was 512.

2.7 Statistical analysis

For all experimental results, statistical analysis was performed by analysis of variance (ANOVA) with general linear model of the software Minitab (Minitab Inc., Coventry, United Kingdom). The results were compared with respect to Tukey's comparison test having 95% confidence interval and at least three replicates were used. Additionally, the Pearson correlation (α ≤ 0.05) was used to find the correlation coefficients between the different parameters investigated.

3 Results and discussion

3.1 Composition of hard candies

The initial moisture content of a hard candy is important since water effects the glassy state characteristics (Borde et al., 2002). The composition of the freshly produced hard candies were calculated after determining their water content by KF titration. The composition of the hard candies are tabulated in Table 3. The initial moisture content of the candy formulations varied between 2.04%–7.08% (w/w). The moisture interval of hard candies is consistent with the literature findings that the initial moisture content of hard confections between 2% and 5% (w/w) (Ergun et al., 2010). Generally, formulations containing FS maintained a higher moisture content than the 100_S and GS including candies. However, the lowest moisture content (4.97% w/w) belongs to 100:0_FS

TABLE 3 Compositions of hard candies.

Composition (%, w/w)								
Sample	Water	Fructose	Glucose	Maltose	Sucrose	DP_3	DP_4	DP_n
100:0_FS	4.97	38.40	50.81	3.87	0.00	1.21	0.00	0.75
75:25_FS	7.08	25.44	33.65	2.56	29.97	0.80	0.00	0.49
50:50_FS	6.43	15.57	20.60	1.57	55.04	0.49	0.00	0.30
25:75_FS	5.83	7.20	9.53	0.73	76.35	0.23	0.00	0.14
100_S	2.04	0.00	0.00	0.00	97.96	0.00	0.00	0.00
25:75_GS	5.93	0.12	6.15	7.80	73.88	2.27	0.00	3.85
50:50_GS	4.64	0.25	13.09	16.59	52.40	4.84	0.00	8.19
75:25_GS	5.31	0.39	20.51	26.00	27.37	7.58	0.00	12.83
100:0_GS	5.60	0.55	28.76	36.46	0.00	10.63	0.00	18.00

[1]DP_3, DP_4 and DP_n, represent oligosaccharides with three, four and more sugar molecules, respectively.

TABLE 4 Compositions of syrups.

Composition (%)		
Component	Glucose syrup (GS)	High fructose corn syrup (FS)
Water	18.00	30.00
Fructose	0.48	28.29
Glucose	24.98	37.43
Maltose	31.67	2.85
DP_3	9.23	0.89
DP_4	0.00	0.00
DP_n	15.63	0.55

*DP_3, DP_4 and DP_n, represent oligosaccharides with three, four and more sugar molecules, respectively.

candy among the samples having only FS in their formulations. This could be related to the difference in the viscosity of the FS and GS. GS contains a considerable amount of high molecular weight–long chain sugars (DP_3, DP_n) that would increase the system viscosity (Hartel, 2002). In contrast, FS is high in glucose and fructose content and contains almost no higher MW oligosaccharides. Therefore, 100:0_FS candy may have attained a lower viscosity, and this may have resulted in higher water loss during boiling of the mixture. This trend changed when sucrose is introduced into the candy formulations as shown in Table 3. The sample having only sucrose (100_S), had the lowest moisture content as expected since GS and FS contains some amount of water in their structures, 18% and 30% (w/w), respectively (Table 4). Images of developed hard candies were provided in Figure 2.

3.2 Water activity, total soluble solids and glass transition temperature properties

3.2.1 Water activity

Understanding the a_w and TSS properties of hard candy formulations is essential since these properties determine the quality

and shelf life of the products (Ergun et al., 2010). As shown in Table 5, the highest a_w belongs to 100_S (0.80) and addition of any doctoring agent significantly decreased ($p \leq 0.05$) the a_w of the candy formulations. Additionally, GS–sucrose formulations had higher a_w than the FS–sucrose ones ($p \leq 0.05$). These findings are related to the sugar composition and the solubility characteristics of the individual sugar molecules. As the sucrose content was replaced by glucose-fructose coming from either FS or GS, humectant capacity of candies increased and water–sugar interactions enhanced (Hartel et al., 2011). Since fructose is the most water-soluble sugar, high fructose content of FS paved the way for the lower a_w of FS–sucrose formulations (Ergun et al., 2010). In a supportive way, the Pearson correlation coefficient (r) analysis showed a strong negative correlation (r = - 0.89) between the a_w and TSS of FS–sucrose formulations. GS, on the other hand, contains very low levels of fructose but includes high amounts of glucose, maltose and high MW oligosaccharides as shown in Table 4. Generally, the a_w of hard candies is below 0.60 which is not suitable for microbial growth. The a_w of hard candies that contain a doctoring agent in their formulations varied between 0.35 and 0.48. Thus, there is a very low microbial spoilage risk for these samples during storage. In contrast, the 100_S sample has a_w of 0.80 which makes it susceptible to yeast and mold growth (Ergun et al., 2010). Thus, addition of a doctoring agent reduced the microbial risk of the sucrose candies. However, low a_w could be a problem if the RH of the surrounding air is higher than that of the candy (Nowakowski and Hartel, 2002). Therefore, FS or GS containing sucrose hard candies must be stored carefully. The high a_w of 100_S is also a problem in terms of sucrose recrystallization during storage. At such a high a_w level, sucrose molecules will have more mobility to interact with each other and initiate crystallization leading to a grainy texture (Netramai et al., 2018). GS–sucrose hard candies have also a high moisture induced graining risk during storage. The high MW sugars and maltose in GS may form a skin at the candy surface. When this skin absorbs moisture from the environment, moisture is mostly retained at the surface and extensive sucrose crystallization may be observed (Hartel, 2002). On the other hand, FS candies can show more humectancy and sugars interact more intensely with the water molecules leaving less free water to initiate graining. Nevertheless, these samples may show stickiness due to their hygroscopic character (Labuza and Labuza, 2004).
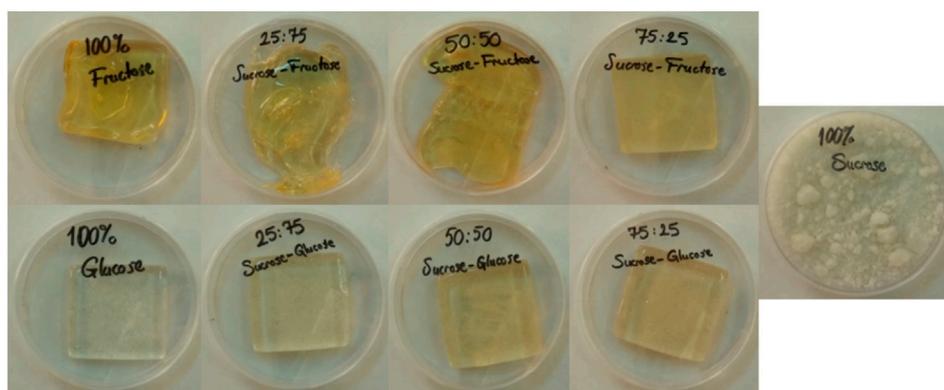
FIGURE 2
Images of developed hard candies.

TABLE 5 Glass transition temperatures, total soluble solids and water activity values of hard candies.

Sample	T_g (°C)	TSS (°Bx)	a_w
100:0_FS	2.13	92.04 ± 0.12[d]	0.41 ± 0.01[c]
75:25_FS	4.03	93.46 ± 0.16[c]	0.35 ± 0.01[d]
50:50_FS	15.21	92.59 ± 0.16[d]	0.41 ± 0.02[c]
25:75_FS	25.61	92.63 ± 0.42[d]	0.37 ± 0.01[d]
100_S	53.32	90.96 ± 0.17[e]	0.80 ± 0.02[a]
25:75_GS	34.30	94.26 ± 0.12[b]	0.42 ± 0.01[c]
50:50_GS	44.02	94.52 ± 0.43[ab]	0.48 ± 0.01[b]
75:25_GS	43.38	90.47 ± 0.40[e]	0.42 ± 0.01[c]
100:0_GS	45.23	95.07 ± 0.17[a]	0.43 ± 0.01[c]

[1]Values represented with different superscript letters at each column are statistically different at $p \le 0.05$. Errors are represented as standard deviations.

3.2.2 Total soluble solids

Solubility characteristics of the sugars in the mixtures also affected the TSS of the hard candies (Zumbé et al., 2001). According to Table 5, addition of a doctoring agent increased the TSS of the candy formulations ($p \le 0.05$). The increase in TSS was more evident with GS addition. Except for the 75:25_GS formulation, GS–sucrose candies maintained a higher TSS profile than FS–sucrose candies ($p \le 0.05$). The main reason was the high total glucose-fructose content of FS–sucrose candies. Solubility of sucrose decreased when the total glucose-fructose content was increased in the system (Bund and Hartel, 2010). As the sucrose content was replaced by corn syrup, sugar molecules competed with each other to interact with water and the supersaturation driving force for sucrose decreased (Hartel et al., 2011). Clearly, glucose and fructose preferentially became soluble in FS–sucrose formulations and sucrose solubility decreased which ended up with lower TSS for FS containing candies. Since GS containing hard candies have much lower total glucose-fructose content, sucrose readily dissolved in these formulations and contributed to the TSS. However, there was an unexpected steep decrease in TSS of 75:25_GS samples. Increasing the GS concentration up to 75% (w/w) in GS–sucrose formulations resulted in the lowest TSS among all formulations ($p \le 0.05$). The reasons behind this behavior at this formulation could be the increase in

both high MW oligosaccharide and glucose-fructose composition of GS–sucrose candies with respect to the other candy formulations having lower GS content (Šmídová et al., 2003). Despite its lower glucose-fructose content with respect to its FS counterparts, GS candies reached the highest total glucose-fructose proportion (~ 21% w/w) at this specific formulation (75:25_GS). Consequently, sucrose solubility may have been restricted for the first time in GS–sucrose formulations. In addition to the lower levels of dissolved sucrose, total concentration of the high MW oligosaccharides also reached its top level in this formulation. In the presence of higher glucose-fructose concentration that shows high solubility, long saccharide chains may have also experienced a lower solubility. Therefore, it is believed that the combined effect of decreased sucrose and high MW sugar solubilities resulted in lower TSS for 75:25_GS candies (Levenson and Hartel, 2005).

3.2.3 Glass transition temperature

Another factor that needs to be considered is the T_g values of the hard candies. 100_S candies showed the highest T_g as 53.32°C whereas addition of FS or GS produced lower T_g values as demonstrated in Table 5. Without any doctoring agent, sucrose molecules were able to interact with each other to form a crystal lattice (McFetridge et al., 2004). As a result, 100_S candies reached the glassy state during cooling

at a higher temperature with respect to other samples. On the other hand, presence of doctoring agents, diminished the degree of interactions between sucrose molecules in the rubbery state in which molecular mobility is sufficient enough to form crystal structures (Hartel et al., 2011). Moreover, the T_g values of GS–sucrose candies were higher than that of FS–sucrose candies mainly due to the presence of higher amounts of maltose and high MW sugars (Ergun et al., 2010). These sugars have high T_g values individually contributing to the increased T_g level of GS containing samples. Contrarily, FS candies have more fructose and glucose concentration having much lower individual T_g values (5°C and 31°C) compared with the T_g of maltose and high MW oligosaccharides (87 and 112°C–180°C) (Liang et al., 2007) (Table 2). The plasticizing effect of water on T_g was apparently observed on FS–sucrose samples since increasing FS concentration (from 25:75_FS to 75:25_FS) increased the water content from 5.83% to 7.08% (w/w) and decreased T_g from 25.61°C to 4.03°C. Although, GS addition to sucrose candies also decreased T_g, there is not a clear trend between GS concentration and T_g values. The reason could be the distortion of the ideal volume mixing behavior of the GS–sucrose systems (Reinheimer et al., 2010). Generally, when a low T_g component is mixed with a high T_g component, the T_g of the system attains a level between the individual T_g values of the mixed components. However, mixing of two high T_g components may not show an ideal mixing behavior (Šmídová et al., 2003). Since T_g values of GS components are higher than those of FS components, improper mixing may have occurred in GS containing formulations. Moreover, addition of high MW compounds to another component induces a broader glass transition range that would lead to a high variability in calculated T_g values (Kawai et al., 2019). This could be the case in GS–sucrose hard candies that revealed variable T_g values at different GS concentrations.

The T_g results showed that the doctoring agents (FS and GS) clearly decreased sucrose crystallization taking place in the rubbery state during the cooling period. It should also be noted that, T_g values of the FS–sucrose candies remained below the room temperature except for the 25:75_FS sample (Table 5). This is quite risky since such T_g values may lead to temperature induced internal graining during storage (Liang et al., 2007). GS samples, on the other hand, possess higher levels of T_g reducing the risk of temperature induced sucrose crystallization (Levenson and Hartel, 2005). However, GS - sucrose candies are more prone to moisture induced surface graining than FS - sucrose candies as previously discussed when explaining a_w results. Although GS candies would absorb less moisture with respect to FS candies at high RH storage conditions due to their higher a_w, the free water population would be higher in GS candies in the absence of a sufficient humectant content (Hartel et al., 2011). FS candies would suffer less from the moisture induced sucrose crystallization but they may become stickier than GS samples due their increased level of moisture absorption.

3.3 Longitudinal relaxation time and second moment results

3.3.1 Longitudinal relaxation time

T_1 analysis of hard candies showed a monoexponential relaxation behavior except for 100_S candies showing biexponential relaxation (Table 6). The monophasic relaxation of FS or GS added candies indicated that components coming from

doctoring agents had enhanced affinity with water and provided a more homogeneous sample (Okada et al., 2019). Additionally, doctoring agents are also able to place themselves between the sucrose molecules and this may have also contributed to the homogeneity of the continuous phase in the hard candies. The presence of solely sucrose probably induced more interactions between the individual sucrose molecules creating distinct proton populations within the samples (Mariette, 2009). The relaxation peaks of 100_S candies exerted a very long T_1 (1,627 ms) and a much shorter (~ 78 ms) components supporting the previous claim. Probably, intense interactions between the sucrose molecules created a non-homogeneous water and sucrose distribution within the samples and locally gathered ordered crystalline sucrose fractions contributed to the long T_1 component (Aso et al., 2007). Besides, T_1 values of hard candies containing doctoring agents showed some differences since spin-lattice relaxation behavior is sensitive to the alterations in the quantity and order of crystalline state (Adam-Berret et al., 2008). Generally, longer T_1 values are observed with compact and highly ordered crystalline state arrangements at high solid concentrations (Adam-Berret et al., 2009). 100_S samples having the highest T_g also attained the longest T_1 which was compatible with the previous claim that related the long T_1 with the higher order of the crystalline state. The addition of doctoring agents extremely lowered the T_1 values in consistence with their sucrose crystallization retarding effect.

3.3.2 Second moment

In addition to T_1, M_2 is also a valuable parameter to understand crystalline state molecular dynamics with more precision as proton mobility within a crystal lattice determines the M_2 of a system. A higher M_2 value is associated with a lower proton mobility in a solid state (Van Duynhoven et al., 2002). The reason behind this behavior is the enhanced dipolar interactions between the protons in lower molecular mobility conditions (Wang et al., 2002). Therefore, higher M_2 values are expected at higher degrees of crystallinity (Grunin et al., 2019). The data in Table 6 indicates this trend as the 100_S candies had the highest M_2 (10.96) indicating that 100_S samples possessed the highest crystallinity level ($p \leq 0.05$). Similar to the T_1 results, incorporation of doctoring agents also reduced the M_2, thus the degree of crystallinity of the sucrose hard candies ($p \leq 0.05$). Addition of 25% (w/w) doctoring agent (GS or FS) decreased the degree of crystallinity and attained similar M_2 levels for both samples (25:75_FS and 25:75_GS). However, when the added syrup content increased to 50% (w/w), GS–sucrose candies demonstrated a higher crystallinity (M_2) than FS–sucrose candies ($p \leq 0.05$). This means 50: 50_GS candies experienced more sucrose crystallization than 50:50_FS candies. However, 50:50_GS candies have a higher T_g than the T_g of 50: 50_FS candies ($p \leq 0.05$). Normally, a higher T_g corresponds to an earlier entrance to the glassy state in which molecular mobility is severely restricted so that almost no sucrose crystallization can take place. A high T_g value is also an indicator of shorter time spent in the rubbery phase where sucrose crystallization is possible during cooling (Roos, 2002). Nevertheless, 50:50_FS candies with much lower T_g showed less crystallinity. Here, the high total glucose-fructose content (~ 35% w/w) of FS predominated the system and retarded the interactions between the sucrose molecules even at the rubbery state during candy production. Glucose and fructose molecules are able to

TABLE 6 Longitudinal relaxation time and second moment results.

Sample	T_1 (ms)				M_2
	Peak 1 (ms)	Peak 2 (ms)	Area 1 (%)	Area 2 (%)	
100:0_FS	101.75 ± 6.43[f]	-	100.00	-	6.85 ± 0.08[e]
75:25_FS	138.95 ± 0.64[c]	-	100.00	-	8.71 ± 0.06[c]
50:50_FS	111.67 ± 0.32[e]	-	100.00	-	8.07 ± 0.04[d]
25:75_FS	121.80 ± 1.99[d]	-	100.00	-	8.91 ± 0.13[c]
100_S	1,627.00 ± 22.61[a]	77.62 ± 5.90	62.00	38.00	10.96 ± 0.19[a]
25:75_GS	115.50 ± 0.53[e]	-	100.00	-	8.76 ± 0.12[c]
50:50_GS	149.20 ± 0.14[b]	-	100.00	-	9.38 ± 0.09[b]
75:25_GS	68.70 ± 1.21[g]	-	100.00	-	5.26 ± 0.17[f]
100:0_GS	123.05 ± 0.78[d]	-	100.00	-	9.01 ± 0.07[c]

[1]Values represented with different superscript letters at each column are statistically different at $p \le 0.05$. Errors are represented as standard deviations.

interact intensively with sucrose molecules via interactions such as hydrogen bonding (Spanemberg et al., 2022). Therefore, sucrose nucleation rate was diminished, and crystal lattice formation was restricted in 50:50_FS samples. On the other hand, the low total glucose-fructose concentration (~ 13.5% w/w) of 50:50_GS samples could not retard the sucrose crystallization taking place in the rubbery state before entering the glassy state, as efficiently as the F50:50_FS samples. In this way, even the time spent in the rubbery state was short, the amount of sucrose crystals formed in this state was high. When the added syrup concentration increased to 75% (w/w), this trend has changed. 75:25_GS candies showed a very low degree of crystallinity whereas 75:25_FS candies attained higher crystallinity levels (Table 6). Although the total glucose-fructose content of GS–sucrose candies was still much lower than the FS–sucrose candies at this concentration, the increased level of high MW sugars clearly predominated the GS candy system. One of the effects of high concentrations of high MW oligosaccharides is the increased system viscosity (Raudonus et al., 2000). The increased viscosity may have compensated the effect of low glucose-fructose content by decreasing the sucrose mobility effectively in the rubbery state (Hartel, 2002). Thus, formation of a crystal lattice by sucrose molecules may have been retarded. Based on these results, it is possible to claim that the type and concentration of syrups added to sucrose candies have distinct effects on the sucrose crystallization properties of hard candy formulations.

In fact, M_2 analysis provided a very important information on the crystallization pattern in hard candies. T_g of the 100_S and 75:25_GS candies are high and close to each other as 53.32°C and 45.23°C, respectively. Therefore, one can assume that both candy formulations may have similar crystallinity properties since both samples reached the metastable glassy state at similar temperature regions during production. However, the crystallization processes taking place in these samples were completely opposite to each other. While 100_S candies experienced the highest sucrose crystallization level, 75:25_GS candies showed much less crystal lattice formation. Consequently, M_2 analysis provided a detailed understanding of the glass transition and crystallization properties of hard candies. Finally, correlations between the NMR and other measured parameters could be mentioned. Strong positive correlations between T_1 - T_g ($r = 0.89$), M_2 - T_g ($r = 0.90$) and T_1 - a_w ($r = 0.99$) have been detected for the FS candies. The only correlation that has been observed for GS candies belonged to the T_1 - a_w with an r of 0.99.

4 Conclusion

This study showed that addition of doctoring agent to sucrose candies reduced the T_g and the level of sucrose crystallization in the hard candies. The type and concentration of the doctoring agent (GS or FS) incorporated into the hard candies affected the sucrose crystallization properties of the hard candies, differently. Moreover, both of the TD NMR parameters, T_1 and M_2 have been successfully used to interpret the glass transition and degree of sucrose crystallization characteristics of the hard candy formulations. Herewith, the direct integration of the fast Fourier-transform of MSE to calculate M_2 could be presented as a precise method to detect the quantity and nature of sucrose crystallization in hard candies.

Data availability statement

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Author contributions

BO: Conceptualization, Project administration, Resources, Writing–original draft, Writing–review and editing. BB: Data curation, Formal Analysis, Investigation, Methodology, Writing–original draft. SU: Data curation, Project administration, Writing–original draft. LG: Conceptualization, Formal Analysis, Investigation, Methodology, Software, Supervision, Writing–review and editing. MO: Conceptualization, Funding acquisition, Investigation, Methodology, Software, Supervision, Writing–review and editing.

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Conflict of interest

Authors SU and LG were employed by Resonance Systems GmbH.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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