Investigating the crystallinity of hard candies prepared and stored at different temperatures with low field-NMR relaxometry

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Abstract

Background: In this study, hard candies were produced by using sucrose, glucose syrup and water. They were cooked at different temperatures, changing from 135 to 145 °C with an interval of 2.5 °C. They were stored at different storage temperatures, which were 25, 4, −18 and −80 °C. Hard candies placed at room temperature were stored for 2 months. In order to understand the crystallization characteristics of the hard candies, time domain (TD) proton nuclear magnetic resonance (^{1}H-NMR) parameters of longitudinal relaxation time (T_1) and second moment (M_2) measurements were conducted. Moisture contents of the hard candies were determined by Karl–Fischer titration. X-ray diffraction experiments were also conducted as the complementary analysis.

Results: Increasing cooking temperature increased the crystallinity and decreased the moisture content of the hard candies significantly ($P \leq 0.05$). Furthermore, storage temperature and storage time had significant effects on the crystallinity of the hard candies ($P \leq 0.05$). The results of T_1 and M_2 correlated with each other ($r > 0.8$, $P \leq 0.5$) and both produced the highest value at the cooking temperature of 145 °C and storage temperature of 4 °C ($P \leq 0.05$). The values of T_1 and M_2 were obtained as 245.9 ms and 13.0×10^{-8} Hz^2, respectively, for the cooking temperature of 145 °C and storage temperature of 4 °C.

Conclusion: This study demonstrated that the crystallinity of hard candies can be observed and examined by TD-NMR relaxometry, as an alternative to commonly used methods.

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Supporting information may be found in the online version of this article.

Keywords: hard candy; crystallinity; moisture content; ^{1}H-NMR; second moment; T_1

INTRODUCTION

Hard candies, or glassy confections, are amorphous confections made from the mixture of a sweetener and doctoring agents. While the sweetener used is mostly sucrose, corn syrup is mostly preferred as the doctoring agent. Subsequently, additional water is mixed with these ingredients and the resulting mixture is heated to produce a concentrated mixture. Then, it is cooled down to below its glass transition temperature (T_g) to reach glassy state.[1] In the glassy state, the product is considered stable at least for some interval because the molecular mobility is restricted. However, the glassy state is not a thermodynamically stable state, but it is a kinetically stable state.[2] Thus, some slow changes such as crystallization of sucrose can still occur in hard candies.[3] Doctoring agents such as glucose syrup have a significant amount of simple sugars that can be incorporated between the sucrose molecules and interfere with the crystal lattice formation of the sucrose molecules.[4] Crystallization in hard candies can be prevented by controlling the environmental conditions.[3] However,

controlling the environmental conditions such as relative humidity (RH) is not always easy. Therefore, changes in temperature can be considered to produce products with different crystallization properties.[5] For instance, changing cooking temperature may affect the interactions of the sucrose molecules resulting in different amorphous behaviour (glassy characters) in hard candies.

Production of hard candy is usually performed at very high temperatures (135–160 °C). Even a slight temperature change affects the quality of the hard candy. Therefore, cooking temperature is

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very important for selecting the quality parameters. Changing cooking temperature affects both the moisture content and the crystallinity of the hard candies. Increasing cooking temperature results in higher moisture loss and a highly concentrated solution. When the saturation of the solution increases, the rate of crystallization also increases during the cooling process.[6]

Another important quality parameter is moisture content of the candies, which is essential for determining the shelf-life of the hard candy. Moisture content affects the textural properties since water plays an important role in the stickiness. In terms of crystallization, cooling rate is a very important factor. When the cooking temperature is increased, the cooling rate decreases due to increased cooling time resulting in a more crystalline candy. The desired situation for hard candies is to have a less crystalline and more amorphous product. So, the cooking and cooling processes are very important to have a glassier candy. As a result, to have a good quality candy, the cooking temperature should be selected properly.[6]

There can also be some undesirable physicochemical changes in the glassy state of hard candies during storage. These changes are undesirable because the final product would have unacceptable textural and sensorial properties.[7] The two main causes for hard candy deterioration during storage are water migration and temperature difference. If the hard candy is placed into an environment where the RH is higher than the water activity (a_w) of the hard candy, the moisture content of the sample can increase due to moisture absorption from the environment.[8] As a result of water absorption, T_g can decrease below the storage temperature since water acts as a plasticizer. Thus, molecular mobility of the system increases.[9] Candies can become sticky, or experience sucrose crystallization based on the candy characteristics.[10] If the formulation of candy consists of a large amount of glucose and fructose, there would be an extreme water absorption because of the hygroscopic characteristics of glucose and fructose. This can result in a sticky product.[11] When candy has a high sucrose concentration, water absorbed by the product can be lower but the water in the candy can have higher mobility due to the absence or low level of humectants. Therefore, free water can be used by sucrose and then sucrose can recrystallize. In general, for this kind of product, crystallization starts from the surface and it continues into the interior as time passes.[12] Stickiness cannot be observed in these hard candies but lower sensorial and textural properties can be observed because of extreme graining. Thus, an adjustment should be made between graining properties and stickiness by controlling the storage conditions, that is, storage temperature and RH.[1]

The glass transition process is the most crucial phase in the hard candy production. At T_g, hard candy can experience various changes. These changes can be both in physicochemical and mechanical properties such as molecular mobility, specific heat capacity (c_p), viscosity, dielectric constant, and hardness.[13] Exploring the glass transition process is very important since the main aim of the cooling of the hard candy mixtures is to obtain a glassy state in which most of the physicochemical changes are limited.[9] The glassy state should be obtained for each candy because shelf life of the products depends on the glassy state.[14] Differential scanning calorimetry (DSC) is one of the classical methods which is used for measuring the glass transition process and identifying the T_g. There is a positive correlation between T_g and crystallinity degree. Thus, it can be used for examining the degree of crystallinity of the glassy products.[15]

One of the methods used for crystallinity measurement is X-ray diffraction (XRD), but the peak selection may cause some errors in the obtained results. Moreover, mixed systems such as hard candies can produce broad peaks which cannot be easily distinguished from each other.[16] Fourier-transform infrared (FTIR) spectroscopy may also be considered for crystal content measurements. However, it has some limited moisture range specifications preventing the analysis of the samples.[17] Another alternative method is microscopy, but the sample should be transparent and have low density matrix which is not appropriate for hard candy samples.[18] However, low-field nuclear magnetic resonance (LF-NMR) relaxometry can determine the crystal content and degree of crystallinity in an easy and fast way.[19] Free induction decay (FID) with a single pulse and the consecutive proton relaxation data are used to differentiate solid and liquid fractions of a material.[20] Nevertheless, just applying FID leads to loss of signal obtained by the solid part due to the 'dead time' phenomenon which is created by the delay in the record of the signal by the receiver.[19] However, solid echo (SE) sequence enables the detection of the larger part of the signal coming from the solid fraction. The evident approach of fitting of SE decays with classical Abrahamian or Pake functions brings usage of multiple approximation parameters and their possible ambiguous interpretation.[21,22] In this way, the second moment (M_2) fundamentally occurs proportional to crystalline content and can be simply calculated in different ways, in particular, just by the direct integration of the NMR spectrum.[21] In addition to M_2 measurements for the evaluation of degree of crystallinity of hard candies, longitudinal relaxation time (T_1) can also be used for the same purpose. The T_1 is determined by performing saturation recovery (SR) or inversion recovery (IR) sequences.[23] Le Botlan *et al.* have used T_1 to explore and quantify the crystallinity of different sugars.[16]

In this study, we evaluated the moisture content and crystallinity characteristics of hard candies cooked at different temperatures. Moreover, the effects of storage time and storage temperature were also analysed. Moisture content, total soluble solids (TSS), XRD, DSC and time domain (TD)-NMR measurements were conducted to analyse the physicochemical properties of the candies at the glassy state. It is hypothesized that the changing cooking temperature would significantly affect the moisture content and thus, crystallinity of the hard candies. Different storage time and storage temperatures were also applied to observe any possible effects on the crystallinity of the samples. The use of SE sequence could be a useful tool to monitor the degree of crystallinity of hard candy samples right after the production since it is capable of providing the full acquisition of the solid signal from the sample. The potential of LF-NMR parameters (M_2 and T_1) was investigated for the monitoring of crystallinity of the hard candy formulations.

MATERIALS AND METHODS

Sample preparation

In order to prepare hard candy samples; sucrose, glucose syrup, and water were used. The amounts of glucose syrup with Brix 85°, sucrose and water were 430, 470 and 100 g/kg, respectively. Ingredients were mixed. Then, the mixture was boiled up to high temperatures in a vacuum cooker. Cooking temperature ranged between 135 and 145 °C with an interval of 2.5 °C. Next, the boiled mixture of hard candy was poured into moulds. After pouring, all samples were cooled down until they reached room temperature. For each cooking temperature, the same procedure

was applied. Samples which were stored at room temperature were divided into two sets. The first set was kept at room temperature for 2 days. The second set was kept at room temperature for 2 months.

Other samples were initially kept at room temperature for 2 months. Following these 2 months, they were kept at different storage temperatures for 3 days which are 4, −18 and −80 °C. RH of these environments were controlled during the storage. RH of 25 and 4 °C environments were 52% and 38%, respectively. Other environments had a RH which was near to zero. The aim of using different storage temperatures was to produce a crystalline phase in hard candies and, if any, detect this phase with LF-NMR relaxometry.

Water properties of hard candy formulations

Karl–Fischer titration method was used for the determination of moisture content of hard candies since they have low moisture content.[1] The experiment was performed by a Karl–Fischer Titrator (TitraLab KF1000 Series; HACH, Manchester, UK) at 25 °C with three replicates.

Total soluble solids (TSS)

TSS values of the fresh hard candies were determined by using the solid refractive index method (ATC 0-90 Refractometer; AKYOL Instruments, Istanbul, Turkey). Freshly produced samples were put on top the refractometer and the value was read by looking from the binocular.

TSS values of the stored hard candies were determined by using the refractive index method (HI 96801 Refractometer; HANNA Instruments, Woonsocket RI, USA).[2] Hard candy samples were dissolved in water with a specified dilution ratio which was 1:5. The experiment was conducted at room temperature and samples were stirred for 3 h. After stirring, a measurement was taken by dripping the solution on the refractometer. Three replicates were used.

X-ray diffraction (XRD) analysis

XRD analysis was conducted for hard candy samples [Middle East Technical University (METU) Central Laboratory, Ankara, Turkey].
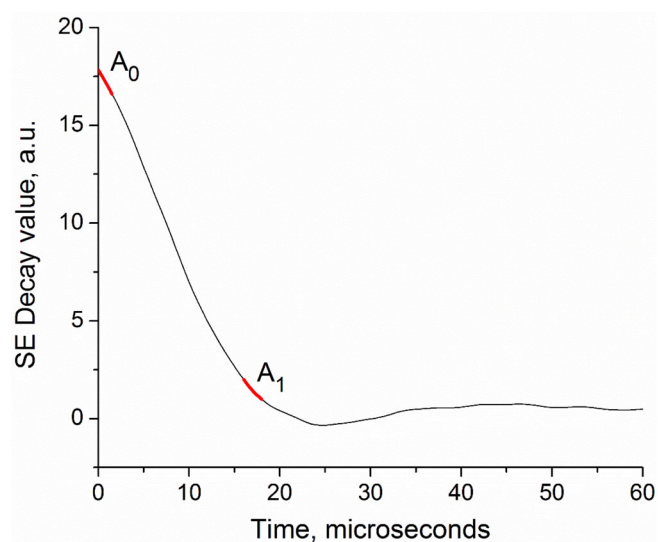

Figure 1. Representative solid echo (SE) signal showing the different contributions.

Samples were broken into pieces to obtain a powder form of the hard candies. The sampling width, scan axis, scan range, and scan speed were 0.02°, 2θ, 3°–80°, and 2°/min, respectively (Rigaku Ultima-IV XRD Device; Rikagu Corporations, Tokyo, Japan).

Differential scanning calorimetry (DSC) analysis

DSC analysis was also conducted for hard candy samples (METU Central Laboratory). Similar to procedure that was applied in XRD analysis, samples were broken into small pieces to obtained a powder form of the hard candies. Temperature range was between −40 °C and 120 °C. Heating rate was selected as 10 °C/min (Perkin Elmer Diamond DSC; Perkin Elmer, Waltham, MA, USA).

Time domain nuclear magnetic resonance (TD-NMR) 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. Samples were put into the tubes that have a diameter of 10 mm. These tubes were placed into the magnet. Then, the measurements were done. For different type of measurements such as T_1 and M_2, different sequences were used.

Longitudinal relaxation time (T1) measurements

A SR sequence having a relaxation period of 2 s and a delay time between 1000 and 1500 ms for 16 points was used with four scans to measure T_1. Mono- and multi-exponential fittings of the relaxation spectra were carried out by the Relax8 software package (Resonance Systems GmbH).

Second moment (M2)

The M_2 values were obtained by the SE sequence having 10 s repetition delay, 4 ms echo delay and 32 scans. Relax8 (Resonance Systems GmbH) 'Solid Lab' module was used to calculate M_2 values. Number of points that were used for FID was 512.

The principle of the M_2 calculation via 'averaging of FID regions' is based on the assumption that the apparent spin–spin relaxation time of the crystalline structures is shorter than the one in the amorphous areas of the same sample, due to smaller averaged inter-hydrogen distance and less mobility in denser packed crystallites. The method implemented in the module uses the averaged transverse relaxation decay value on top A_0 (at the zero-time point – this value contains both crystalline and amorphous signal amplitudes) and at the selected time as A_1, in the case of this research the value was chosen around 17 μs (as suggested by Grunin et al.[24] since the patterns of hard candy FID behaves very similar to the FIDs of cellulose), where the amorphous FID contributes more into the signal than the crystalline protons due to the mentioned relaxation time difference (Fig. 1). Then the parameter ξ of crystallinity (and the M_2) is calculated proportionally to $\xi \sim (A_0 - A_1)/A_0$ and, finally, the module is calibrated by the simulated model signals with known M_2.

Statistical analysis

For all experimental results, analysis of variance (ANOVA) was performed using Minitab (Minitab Inc., Coventry, UK). Results were compared according to Tukey's comparison test having 95% confidence interval. Moreover, Pearson correlation ($\alpha \leq 0.05$) was used to find the correlation coefficients between the different parameters examined.

RESULTS AND DISCUSSION

Moisture content

Moisture content is an important factor for the physical characteristics of hard candies. Moisture migration is a diffusion process, and it is affected by the concentration difference.[25] Moisture content results are shown in Table 1. Moisture content of the hard candies changed significantly when the cooking and storage temperatures were changed ($P < 0.05$). When the cooking temperature is increased, the rate of evaporation also increases. This results in a lower moisture content hard candy.[6] Thus, moisture content of hard candies decreased when the cooking temperature was increased from 135 to 145 °C and results confirmed this trend. Similarly, decreasing storage temperature also resulted in lower moisture contents. The lowest moisture content values were obtained for the samples stored at −80 °C. When the storage temperature was 25 °C, hard candies gained moisture during storage. However, when the storage temperatures were in the range of 4, −18 and −80 °C, hard candies probably lost moisture to the surrounding air because the storage environment nearly had zero RH.[26]

Longitudinal relaxation time (T_1)

The T_1 measurements of hard candy are important for both moisture content and crystallinity analysis. As demonstrated in Table 2, hard candies cooked at different temperatures and stored at different temperatures showed significantly different T_1 values. According to the fresh sample measurements, it can be stated that increasing cooking temperature resulted in longer T_1 values.[16] Except for the samples stored at 25 °C, all other samples stored at different temperatures showed the same trend with fresh samples. Samples stored at 25 °C showed their

highest T_1 value at cooking temperature of 140 °C. This may be because the hard crack temperature has been reached. Hard crack temperature is the temperature where a hard candy loses nearly all of its water content. According to the results of the samples stored at 25 °C, the difference between 135 and 140 °C was double of the difference between the cooking temperatures of 140 and 145 °C. Thus, it is likely that after reaching the cooking temperature of 140 °C, hard candy became more stable since hard crack temperature was passed. A similar trend was also observed for the samples at all other storage temperatures. Moreover, storage temperature also affected the T_1 values. When the effect of storage temperature on T_1 was evaluated, it was realized that decreasing storage temperature had an increasing effect on T_1 values. For each cooking temperature, a Tukey comparison test was applied. Results showed that storage temperatures of 4, −18 and −80 °C increased the T_1 values. However, storage temperature of 25 °C decreased the T_1 values. Since hard candies were at the glassy state, the decrease in moisture content resulted in longer T_1. This result showed that T_1 was a suitable parameter to investigate the solid-state relaxation properties of such low moisture products.[27]

Second moment (M_2)

The M_2 is a parameter which is used for crystallinity evaluation. Based on the results presented in Table 3, both changing cooking and storage temperatures significantly ($P \leq 0.05$) affected the M_2 values. When the cooking temperature was increased, M_2 values also increased. Higher cooking temperatures caused more moisture loss from the hard candy samples as previously explained. Thus, candy mixtures became more concentrated. Additionally, they cooled down more slowly due to the increased cooling time.

Table 1. Moisture content results for all measurements

Cooking temperature (°C)	Fresh samples (%)	Samples stored at 25 °C (%)	Samples stored at 4 °C (%)	Samples stored at −18 °C (%)	Samples stored at −80 °C (%)
135	4.8 ± 0.1[a,B]	5.1 ± 0.2[a,A]	4.0 ± 0.3[a,D]	4.4 ± 0.1[a,C]	3.9 ± 0.1[a,D]
137.5	4.1 ± 0.2[b,B]	4.3 ± 0.1[b,A]	3.9 ± 0.1[a,C]	4.4 ± 0.1[a,A]	3.7 ± 0.1[b,D]
140	3.4 ± 0.23[c,C]	3.6 ± 0.2[c,B]	3.5 ± 0.3[b,BC]	3.8 ± 0.1[b,A]	3.0 ± 0.2[c,D]
142.5	3.3 ± 0.2[c,C]	3.5 ± 0.3[c,B]	3.4 ± 0.1[b,B]	3.6 ± 0.1[c,A]	2.9 ± 0.3[cd,D]
145	3.3 ± 0.1[c,B]	3.5 ± 0.4[c,A]	3.0 ± 0.1[c,C]	3.4 ± 0.1[d,A]	2.8 ± 0.1[d,D]

Note: Errors are represented as standard deviations. Lowercase superscript letters represent the comparison test between the column elements. Uppercase superscript letters represent the comparison between the row elements.

Table 2. Longitudinal relaxation time (T_1) results for all measurements

Cooking temperature (°C)	Fresh samples (ms)	Samples stored at 25 °C (ms)	Samples stored at 4 °C (ms)	Samples stored at −18 °C (ms)	Samples stored at −80 °C (ms)
135	165.8 ± 2.0[d,C]	153.0 ± 12.5[e,D]	176.1 ± 7.6[d,A]	172.8 ± 3.4[e,B]	171.8 ± 2.7[d,B]
137.5	179.9 ± 9.0[c,C]	169.3 ± 5.6[d,D]	193.1 ± 0.7[c,A]	185.5 ± 6.2[d,B]	194.0 ± 2.8[c,A]
140	199.3 ± 13.5[b,D]	211.4 ± 11.1[a,C]	217.2 ± 0.5[b,B]	215.2 ± 1.3[c,BC]	225.5 ± 6.7[b,A]
142.5	207.8 ± 15.9[ab,C]	174.3 ± 6.6[c,D]	220.3 ± 3.8[b,B]	222.6 ± 6.7[b,B]	228.6 ± 2.5[b,A]
145	209.5 ± 15.4[a,C]	185.4 ± 5.7[b,D]	245.9 ± 5.4[a,A]	243.5 ± 3.1[a,B]	243.6 ± 6.8[a,B]

Note: Errors are represented as standard deviations. Lowercase superscript letters represent the comparison test between the column elements. Uppercase superscript letters represent the comparison between the row elements.

**Table 3.** Second moment ($M_2 \times 10^8$ Hz^2) results for all measurements

Cooking temperature (°C)	Fresh samples	Samples stored at 25 °C	Samples stored at 4 °C	Samples stored at −18 °C	Samples stored at −80 °C
135	11.9 ± 0.0^{c,B}	11.6 ± 0.3^{d,C}	12.1 ± 0.0^{d,A}	12.2 ± 0.1^{d,A}	12.2 ± 0.1^{d,A}
137.5	12.2 ± 0.0^{b,B}	11.9 ± 0.3^{c,C}	12.4 ± 0.1^{c,A}	12.4 ± 0.0^{c,A}	12.4 ± 0.0^{c,A}
140	12.6 ± 0.0^{a,A}	12.7 ± 0.4^{a,A}	12.7 ± 0.0^{b,A}	12.7 ± 0.1^{b,A}	12.7 ± 0.1^{b,A}
142.5	12.6 ± 0.1^{a,A}	12.1 ± 0.4^{b,B}	12.7 ± 0.1^{b,A}	12.7 ± 0.0^{b,A}	12.8 ± 0.1^{b,A}
145	12.7 ± 0.0^{a,C}	12.2 ± 0.5^{b,D}	13.1 ± 0.0^{a,A}	13.0 ± 0.1^{a,A}	12.9 ± 0.0^{a,B}

Note: Errors are represented as standard deviations. Lowercase superscript letters represent the comparison test between the column elements. Uppercase superscript letters represent the comparison between the row elements.
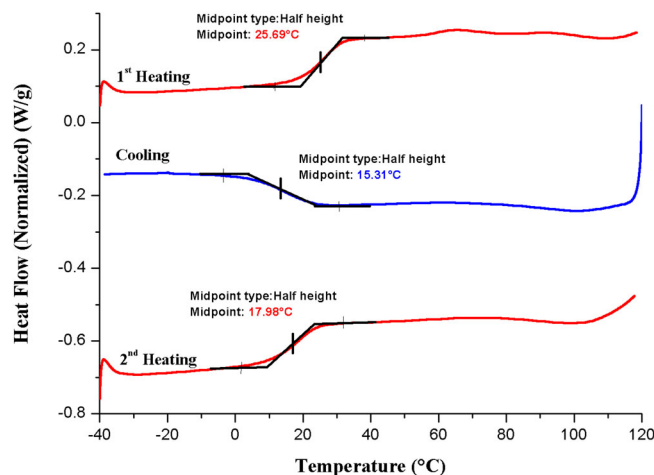
Table 4. Total soluble solids (TSS) results for all measurements

Cooking temperature (°C)	Fresh samples (deg)	Samples stored at 25 °C (deg)	Samples stored at 4 °C (deg)	Samples stored at −18 °C (deg)	Samples stored at −80 °C (deg)
135	82–83	18.8 ± 0.0^{a,A}	16.2 ± 0.0^{c,C}	15.9 ± 0.0^{c,D}	17.0 ± 0.0^{b,B}
137.5		17.9 ± 0.0^{c,A}	15.4 ± 0.0^{d,C}	16.6 ± 0.0^{b,B}	16.7 ± 0.0^{c,B}
140		18.8 ± 0.0^{a,A}	16.5 ± 0.0^{b,B}	16.7 ± 0.0^{b,B}	16.7 ± 0.0^{c,B}
142.5		18.2 ± 0.0^{b,A}	16.6 ± 0.0^{b,B}	16.7 ± 0.0^{b,B}	16.6 ± 0.0^{c,B}
145		18.7 ± 0.0^{a,A}	17.0 ± 0.0^{a,C}	16.9 ± 0.0^{a,C}	17.4 ± 0.0^{a,B}

Note: Errors are represented as standard deviations. Lowercase superscript letters represent the comparison test between the column elements. Uppercase superscript letters represent the comparison between the row elements.
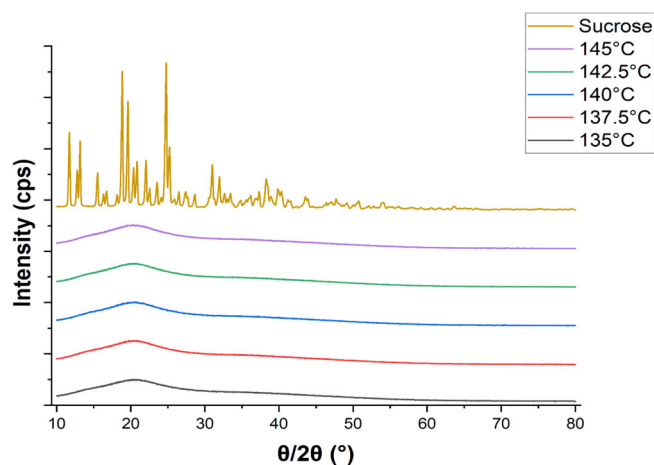
Figure 2. X-ray diffraction (XRD) curves for the hard candies cooked at different temperatures (135, 137.5, 140, 142.5, 145 °C) and stored at the temperature of 25 °C.

Figure 3. Differential scanning calorimetry (DSC) curve for the hard candies cooked 135 °C and stored at −80 °C.

According to the previous findings, decreased rate of cooling resulted in increased crystallization rate.[6] Accordingly, samples cooked at 145 °C generally showed the highest M_2 values, thus crystallinity ($P \leq 0.05$). Storage temperatures of 4, −18 and −80 °C showed the same trend with the fresh sample in terms of cooking temperature. However, storage temperature of 25 °C did not show the same trend. The highest M_2 value was obtained at cooking temperature of 140 °C for the samples stored at 25 °C. As previously discussed for T_1 results in the previous section, the reason for this again may be the hard crack temperature. When the M_2 difference between the cooking temperatures of 135 °C and 140 °C was calculated, it was more than double of the M_2

difference between the cooking temperatures of 140 °C and 145 °C. This trend was similar to that of T_1 results. This can only be explained by the hard crack temperature occurrence.[28] Besides cooking temperature, decreasing storage temperature resulted in higher M_2 values. This was also the case for the T_1 results. These parallel results between the M_2 and T_1 were expected since M_2 and T_1 generally show strong positive correlations.[16] All sugars present in the hard candies probably experienced a decrease in solubility at low temperature conditions. This was also in line with the TSS results of the samples since a higher degree of crystallinity is possible when the solubility of a sugar in the mixture substantially decreases.[29]

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Total soluble solids (TSS)

TSS is another important parameter for the hard candies. As shown in Table 4, the TSS values of fresh samples were measured with refractometer while they were in solid form, but other samples were diluted and then measurements were performed. Increasing the cooking temperature significantly increased the TSS values ($P \leq 0.05$) except for the samples stored at 25 °C. When the cooking temperature increased, moisture loss increased as well. Thus, more concentrated samples were obtained, and this was probably the main reason for the increase in TSS of the majority of the hard candy samples at higher cooking temperatures.[6] However, samples stored at 25 °C demonstrated a stable TSS profile with changing cooking temperatures. Moreover, TSS values of the samples stored at 25 °C were also higher ($P \leq 0.05$) than the other hard candy samples stored at lower temperatures. At low temperature environments (4, −18 and −80 °C), sucrose present in the hard candies may have been utilized for crystallization. According to the results obtained for M_2 (Table 3), which was discussed in the previous section, decreasing the storage temperature increased crystallinity of hard candies. At this low
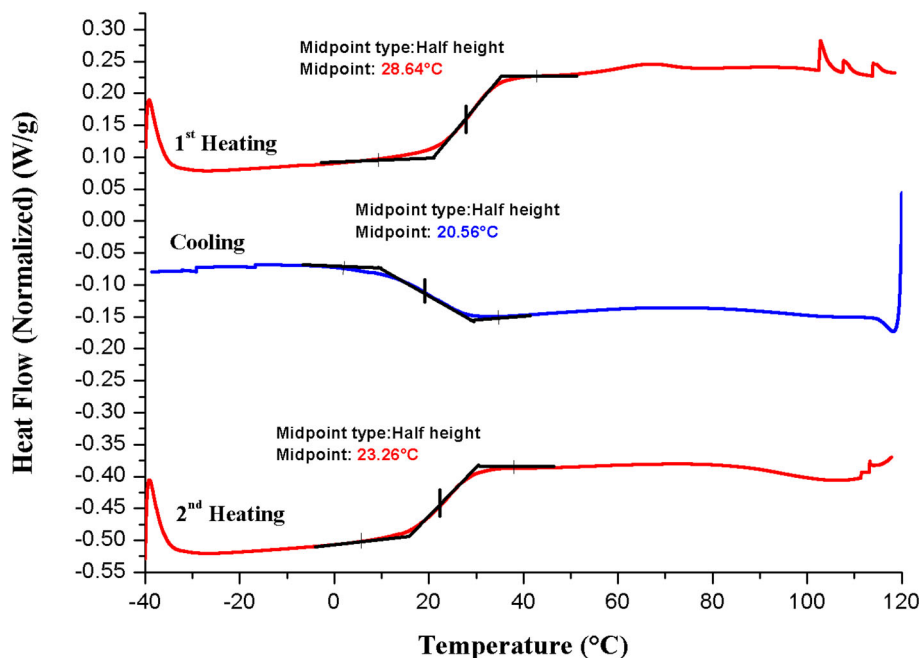

Figure 4. Differential scanning calorimetry (DSC) curve for the hard candies cooked 137.5 °C and stored at −80 °C.
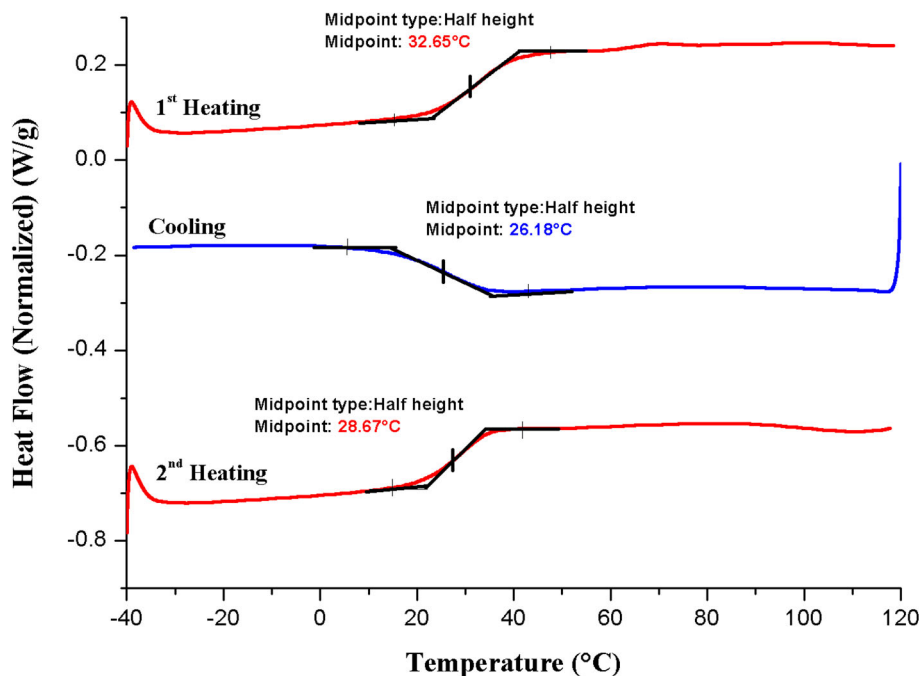

Figure 5. Differential scanning calorimetry (DSC) curve for the hard candies cooked 140 °C and stored at −80 °C.

temperature environment, solubility characteristics of the sugars change. This change results in different TSS values.[30] Therefore, the decrease in solubility or decrease in TSS could be related to the crystallinity properties of the hard candies.

X-ray diffraction (XRD)

XRD is a method used for crystallinity evaluation. Hard candies are amorphous in nature. However, the aim of this study was to evaluate the crystallinity characteristics, if any, of the hard candies. For this reason, XRD analysis was also performed. Only the results for hard candy samples stored at 25 °C are demonstrated in the Fig. 2. When the comparison between hard candy samples and sucrose was made, it could easily be observed that all hard candies showed amorphous behaviour because sucrose had sharp peaks but other samples did not have such sharp and distinct peaks. To see whether storage temperature affects XRD results, XRD analysis was also made for fresh samples and samples stored at −80 °C (Supporting Information Figs S1 and S2). Results
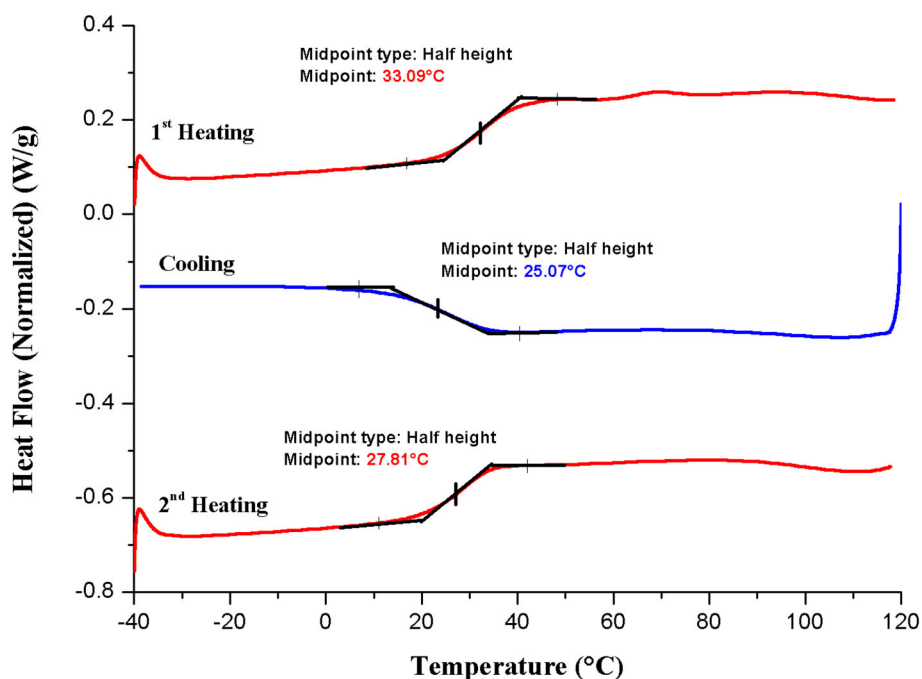

Figure 6. Differential scanning calorimetry (DSC) curve for the hard candies cooked 142.5 °C and stored at −80 °C.
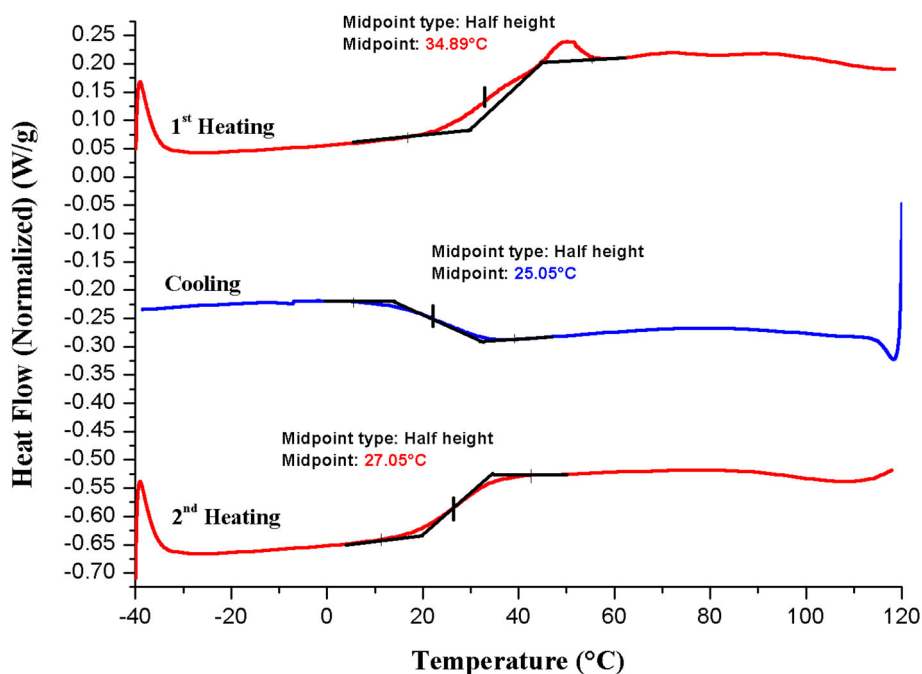

Figure 7. Differential scanning calorimetry (DSC) curve for the hard candies cooked 145 °C and stored at −80 °C.

Table 5. Differential scanning calorimetry (DSC) results for samples stored at −80 °C

Cooking temperature (°C)	First heating T_g (°C)	Cooling T_g (°C)	Second heating T_g (°C)
135	25.69	15.31	17.98
137.5	28.64	20.56	23.26
140	32.65	26.18	28.67
142.5	33.09	25.07	27.81
145	34.89	25.05	27.05

Note: T_g, glass transition temperature.

Table 6. Correlation values for all moisture content, longitudinal relaxation time (T_1) and second moment (M_2) results

	Moisture content of fresh samples (%)	Moisture content of samples stored at 25 °C (%)	Moisture content of samples stored at 4 °C (%)	Moisture content of samples stored at −18 °C (%)	Moisture content of samples stored at −80 °C (%)
T_1 (ms)	−0.983	−0.746	−0.989	−0.982	−0.984
M_2 (× 10^{-8} Hz^2)	−0.993	−0.791	−0.976	−0.951	−0.989

for fresh samples and samples stored at −80 °C also showed amorphous behaviour. However, M_2 values showed that there were also minor crystalline parts in these hard candies. XRD could not detect these minor crystalline regions/crystal particles because it is a method based on macro size.[31] However, M_2 measurement which was performed by TD-NMR relaxometry focused on molecular size rather than the macro size level.[32] In this way, TD-NMR relaxometry provided some information on the crystallinity characteristics of the hard candies.

Differential scanning calorimetry (DSC)

DSC is a method used for T_g determination. The value of T_g is important for both amorphous and semi-crystalline materials. Hard candies mostly have an amorphous structure. For this reason, DSC analysis was performed. Only the results for hard candy samples stored at −80 °C were demonstrated in Figs 3–7. The T_g values of these samples are shown in Table 5. As it can be seen in Table 5, increasing cooking temperature caused T_g values to increase as well. Increased T_g has a positive correlation with crystallinity degree.[15] Thus, T_g results correlate with the M_2 results since increasing cooking temperature also caused M_2 values to increase proportional to crystallinity degree.

Correlations

Pearson correlation test was applied to all related results. As shown in Table 6, almost all correlation values were higher than 0.85 indicating strong correlations.[33] Moisture content values showed correlation with T_1 values. Normally, when the cooking temperature was increased, moisture content values decreased, and this should have resulted in lower T_1 values. However, T_1 values increased due to the crystal formation. The T_g values proved this phenomenon since they were also correlated with T_1 values. When the correlation values between the moisture content and T_1 values were evaluated, it could be concluded that storage temperature had a positive effect on the correlations except for 25 °C. The most possible reason for this low correlation value at 25 °C can be again the hard crack temperature.[32] At this temperature, moisture content was lowered but T_1 value increased

Table 7. Correlation values for samples stored at −80 °C

	Moisture content (%)	T_1 (ms)	M_2 (× 10^{-8} Hz^2)
T_g (°C)	−0.984	1	0.996

Note: T_g, glass transition temperature; T_1, longitudinal relaxation time; M_2, second moment.

because of the crystallization process.[16] However, correlation values of T_g values are given in Table 7. The T_g values showed a perfect correlation with T_1 values. Its correlation with moisture content and M_2 values were also significantly high. As stated before, T_g is related with crystallinity degree. Consequently, T_1 and M_2 results provided a more realistic framework for the low moisture systems, such as glassy state-hard candies studied in this article.

CONCLUSION

This study showed that increasing cooking temperature during hard candy production decreased the moisture content values of the hard candies. Additionally, higher cooking temperatures increased the T_1 and M_2 values of the hard candy samples. This increase in T_1 and M_2 values was related to the degree of crystallinity. Thus, it can be concluded that increasing cooking temperature also increased the crystallinity of hard candies. Another part of this study was to evaluate the effect of storage temperature on crystallinity of hard candies. Results showed that decreasing storage temperature caused a decrease in the moisture content of hard candies and an increase in T_1 and M_2 values. In this way, decreasing storage temperatures also increased the crystallinity degree of the hard candies. TD-NMR relaxometry was able to detect the low amount of crystalline phase within the hard candies. Therefore, TD-NMR relaxometry parameters showed their potential to detect small crystalline fractions which cannot be detected by traditional XRD measurements.

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CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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