Exploring the Correlation of LF NMR Relaxation with the Composition Based Glass Transition

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Abstract

Hard candies produced by 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 (Tg), total soluble solids (TSS) content and water activity (aw). Additionally, time domain (TD) 1H NMR parameters of longitudinal relaxation time (T1) and second moment (M2) measurements have been used to understand the glassy state and crystallization characteristics of different hard candy formulations. Prepared candies include sucrose as the main sugar component and different levels of doctoring agents have been mixed with sucrose to obtain products with different characteristics. Results showed that addition of any doctoring agent to sucrose formulations decreased the Tg of the system significantly ($p \leq 0.05$). Furthermore, GS or FS addition also induced significant changes in TSS and aw of the samples. T1 and M2 results were almost parallel to each other, both produced the highest values at the highest sucrose concentration ($p \leq 0.05$). This study demonstrated 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.

Materials & Methods

SpinTrack, Resonance Systems

- NMR experiments were performed by using a instrument a 20.34 MHz 10 mm r.f. coil NMR system (Spin Track SB45, Kirchheim U.Teck, Germany)).
- Saturation Recovery ➡ T_1 (ms/s)
  Magic Sandwich Echo ➡ M_2
  DSC ➡ Tg

Water Acitivity

Differential Scanning Calorimetry

Total Soluble Solids (TSS)

Sample Preparation

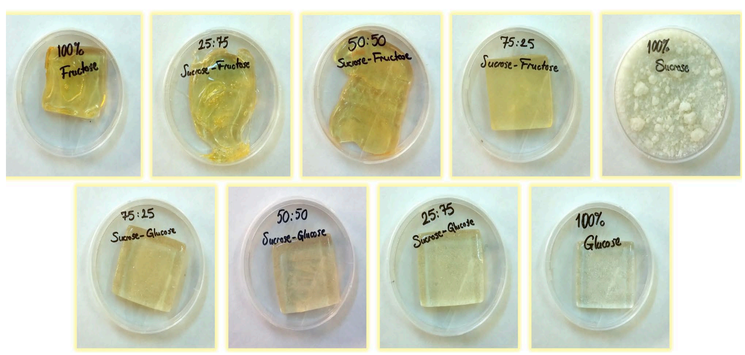

Figure 1. Hard Candies with different formulations

Results

Table 1. T_g , TSS and aw 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}

- Highest aw :100_S. Addition of any doctoring agent decreased aw. GS – sucrose formulations had higher aw than the FS – sucrose. Addition of a doctoring agent increased the TSS. The increase in TSS was more evident with GS addition. GS – sucrose candies : higher TSS profile than FS – sucrose candies (Except for the 75:25_GS formulation). 100_S :the highest Tg as 53.32 °C . Addition of FS or GS produced lower Tg values. The Tg values of GS – sucrose candies were higher than that of FS. Although, GS addition to sucrose candies also decreased Tg, There is not a clear trend between GS concentration and Tg values. The Tg results showed that the doctoring agents (FS and GS) clearly decreased sucrose crystallization taking place in the rubbery state during the cooling period.

Table 2. T_1 and M2 values of hard candies

Sample	T_1 (ms)	M_2
100:0_FS	101.75±6.43^{f}	6.85±0.08^{e}
75:25_FS	138.95±0.64^{c}	8.71±0.06^{c}
50:50_FS	111.67±0.32^{e}	8.07±0.04^{d}
25:75_FS	121.80±1.99^{d}	8.91±0.13^{c}
100_S	1627.00±22.61^{a}	10.96±0.19^{a}
25:75_GS	115.50±0.53^{e}	8.76±0.12^{c}
50:50_GS	149.20±0.14^{b}	9.38±0.09^{b}
75:25_GS	68.70±1.21^{g}	5.26±0.17^{f}
100:0_GS	123.05±0.78^{d}	9.01±0.07^{c}

- T1 has monoexponential relaxation behavior except for 100_S. The relaxation peaks of 100_S candies exerted a very long T1 (1627 ms) and a much shorter (~78 ms). Generally, longer T1 values are observed with compact and highly ordered crystalline state arrangements at high solid concentrations.100_S samples having the highest Tg also attained the longest T1 which was compatible with the claim that related the long T1 with the higher order of the crystalline state. Addition of doctoring agents extremely lowered the T1 values in consistence with their sucrose crystallization retarding effect.

- M_2 can be used to understand crystalline state molecular dynamics. A higher M_2 value is associated with a lower proton mobility in a solid state. 100_S candies had the highest M_2 (10.96) means highest crystallinity level. Similar to T_1 results, incorporation of doctoring agents also reduced the M_2, thus the degree of crystallinity of the sucrose hard candies

References

1. Grunin, L.; Oztop, M.H.; Guner, S.; Baltaci, S.F. Exploring the crystallinity of different powder sugars through solid echo and magic sandwich echo sequences. Magn. Reson. Chem. 2019, 57, 607–615, doi:10.1002/mrc.4866.
2. Hartel, R.W.; Ergun, R.; Vogel, S. Phase/State Transitions of Confectionery Sweeteners: Thermodynamic and Kinetic Aspects. Compr. Rev. Food Sci. Food Saf. 2011, 10, 17–32,

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