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# Determination of the Glass Transition Temperature of Food Polymers Using Low Field NMR

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*This study has shown that the low field NMR technique can be used to investigate the glass transition process in the food polymers. It has been demonstrated that the spin–spin relaxation time constant $T_{2S}$ and the spin-lattice relaxation time constant $T_1$ of the tested food polymers (maltodextrin, bread, cake and cracker) changed dramatically when the polymers underwent the glass transition. The approximate temperature at which $T_{2S}$ and $T_1$ changed dramatically, could be easily determined using a bilinear regression model, and was found to be very close to the glass transition temperature found by differential scanning calorimetry (DSC) or thermal mechanical analysis (TMA) in this study or literature. The plasticization effect of water on the polymers, an important phenomenon in the glass transition in polymers, was also observed in this study. The characteristic change in relaxation time constants observed by the nuclear magnetic resonance (NMR) technique was attributed to the segmental motion of polymers varying in different physical states.*



**Keywords:** glass transition; maltodextrin; nuclear magnetic resonance; proton NMR

## Introduction

The glass transition concept used in polymer science has proven useful in the understanding and control of the physico-chemical properties of food systems. The key parameter in the glass transition temperature of polymers is the glass transition temperature or $T_g$, above which glassy polymers transform to the rubbery state. There are many examples found in the literature where the $T_g$ was related to the structural and textural properties, chemical reactions, and microbiological activities in food systems. The measurement of $T_g$ is an important part of such studies. Among the $T_g$ measurement methods available, differential scanning calorimetry (DSC), dynamic thermal analysis (DTA), dynamic mechanical thermal analysis (DMTA) and dynamic mechanical analysis (DMA) are commonly used. However, other methods may be used as complementary techniques or to improve our understanding of the process. For example, the use of electron spin resonance (ESR) and nuclear magnetic resonance (NMR) may help to experimentally validate that the key factor of the glass transition is the change in segmental mobility. Moreover, each method has limitations, for example, in the sensitivity to certain materials, and the sample size used in the measurement.

NMR is a spectroscopic technique based on the magnetic properties of atomic nuclei, and is often used to monitor the motional properties of molecules by detecting the relaxation characteristics of the NMR active nuclei, such as $^{1}H$, $^{2}H$, $^{3}H$, $^{13}C$, $^{17}O$, $^{23}Na$ and $^{31}P$. Since segmental motion is a fundamental factor in the glass transition of polymers (1, 2, 3) NMR, which is capable of measuring the motional properties of molecules, may have strong potential in the study of the glass transition. Several research groups have reported their findings on this subject (4, 5, 6). Rubin *et al*. (5) investigated vitrification in a model carbohydrate system (honey + water) using NMR. They found that there was a loss of the free induction decay (FID) signal due to the increase in viscosity at honey concentrations greater than 50%, and the intensity of FID signal showed two changes in slope at −42 °C and −60 °C in a 50% dilution sample, which correlated to two DSC-observed $T_g'$s. Kalichevsky *et al*. (4, 7–9) and Ablett *et al*. (6), using NMR, studied the spin–spin relaxation characteristics during the glass transition in amylopectin; gluten; gluten with corn oil, caprylin or hydroxycaproic acid; soluble glutenin; gliading; gluten with sucrose, glucose or frucrose; maltotriose; maltoheptaose; pullulan; and gelatin gels. It was found that the behavior of the spin–spin relaxation time of the 'rigid' component was related to the glass transition. These studies show the possibility of using NMR techniques

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in the study of the glass transition. However, there are still lack of consistent results and methods; more investigations on a wider spectrum of materials, and a better understanding of the techniques would aid the development of this methodology. In addition, there have been few studies to investigate the change in the spin-lattice relaxation time in foods and food materials during the glass transition.

The objective of this research was to investigate the possibility of using a low field nuclear magnetic resonance technique to study the glass transition process and to determine the glass transition temperature in food polymers.

## Materials and Methods

*Sample preparation*

In this study, maltodextrin was used as model food system, because its chemical composition is simple and its glass transition temperature is known. With this simple model, the analysis and understanding of the experimental results would be simpler than with complex, real food systems. The technique developed with the model food systems was then tested using three real food systems: bread, cake and cracker.

Maltodextrin with dextrose equivalents of 15 was purchased from Maltrin M150, (Grain Processing Corporation, Muscatine, IA, U.S.A.). Maltodextrin samples with different water contents were prepared for NMR and DSC tests. Dry maltodextrin powder becomes sticky after mixed with water so it was difficult to obtain a uniform mixture of maltodextrin and water using conventional methods. A low temperature mixing procedure was followed to obtain a relatively uniform maltodextrin-water mixture. In this procedure, known amounts of distilled water were sprinkled into liquid nitrogen (about 100 mL) in a mortar to form ice crystals, which were then ground into fine ice powder with a pestle. An appropriate amount of maltodextrin was then added and mixed to obtain a uniform mixture of ice powder and maltodextrin. Additional liquid nitrogen was added to maintain the low temperature during the mixing. The mixture was stored in a freezer for later use. The water content of the samples were determined by drying at 70 °C for 24 h in an oven. Samples were placed into glass test tubes (12 mm in diameter, for NMR) or aluminum pans (TA Instruments, 60 μl, for DSC), sealed and allowed to equilibrate at room temperature for 2 h prior to measurement.

The bread was made using an automatic bread and dough maker (Chefmate Bakery Oven Model CM725, Korea). The formula was: bread flour 558.0, distilled water 408.3, sugar 16.3, dry milk 6.9, salt 6.5 and active dry yeast 4.0 g/kg. The 'basic' setting on the bread maker was used, with a the total processing time of 4 h and 10 min, including 30 min kneading, 145 min rising, and 75 min baking. The baked bread was left to reach room temperature (about 2 h) before measurements. The water content of the bread was 395 g/kg (wet base) determined by drying at 70 °C for 24 h in an oven. The cake formula consisted of 272 g/kg cake flour (Softasilk, General Mills, Minnepolis, MN, U.S.A.), 304 g/kg sugar, 13 g/kg baking powder (Calumet, Kraft Foods, Chicago, IL, U.S.A.) and 411 g/kg distilled water. Before baking, 1 kg of cake batter was made in a Kitchen-aid Model K45 mixer (4.5 L, bowl). A two-stage mixing process was used to make the batter. In the first stage, flour, baking powder and a sugar solution (498.4 g) were mixed for 30 s at speed 1 and then for 3 min at speed 4. The 610 g/kg sucrose solution (dry base, refractive index 1.4441) was made by mixing sucrose and water in a beaker in room temperature and then covered and heated until boiling. In the second stage, 216.6 g of distilled water was added to the batter. The batter was mixed for 30 s at speed 1 and then for 1.5 min at speed 4. 900 g of batter was poured into a $20 \times 20 \times 5$ cm$^3$ Pyrex pan and baked at 190 °C for 70 min in a conventional oven. The cake was left to reach room temperature (about 2 h) before measurement. The water content of the cake was 414 g/kg (wet base) determined by drying at 70 °C for 24 h in an oven. The cracker sample with its $T_g$ value of 47 °C determined by DMTA was provided by a local company.

*NMR experiment*

The 20 MHz PCT 20/30 NMR Analyzer (Process Control Technology, Inc., Ft. Collins, CO, U.S.A.) was used to conduct the NMR investigations. The NMR system was equipped with a temperature control device providing a sample temperature range from −100−120 °C. A fiber-optic temperature sensor was used to measure the actual temperature of the sample at the time when the measurement was taken. Two NMR pulse sequences, the one-pulse sequence (a 90° pulse sequence) and the T1SR ($T_1$ saturation recovery) pulse sequence were used to measure the spin-spin relaxation time and spin-lattice relaxation time, respectively (10).

The free induction decay (FID) curves obtained from the one-pulse experiments were fitted to a two component model (11) which produced two spin-spin relaxation times ($T_{2S}$) and ($T_{2M}$). Only the shorter $T_{2S}$ was used because it was thought that the shorter component was more closely associated with the solid or rigid structure of the polymer (4, 11).

The samples (2.5 g for the maltodextrin sample, and 3.5 g for the cake, bread, and cracker) were weighted into a glass test tube of 12 mm in diameter, sealed and placed into the magnet module of the NMR analyzer for testing.

The temperature range used in the NMR experiment was about ±50 °C of the expected $T_g$ obtained from the literature. Each sample was measured at eight temperature points. The temperature intervals between measured points were about 10 °C−30 °C. At every temperature point, the sample was allowed to equilibrate for 5 min (the change in the sample temperature during this period was within 1 °C) before measurements were taken. For the one-pulse sequence, the measure-

ments of cake, cracker and bread sample were taken at several more temperature points. The experiments were run in duplicate for each sample. The final results are an average of the two runs.

The $T_1$ of maltodextrins samples was also measured at 200 Hz (4.7 Tesla) using the SISCO NMR Spectrometer (SISCO, Inc., Sunnyvale, CA, U.S.A.) to investigate the effect of resonance frequency on $T_1$ measurement.

*DSC experiment*

The DSC measurement for maltodextrin samples was taken using the DSC 7 (The Perkin-Elmer Corporation, Norwalk, CT, U.S.A.). A sample of approximately 20 mg was placed into an aluminum pan and sealed using a DSC pan sealer. The sample was cooled to about 50 °C lower than the expected $T_g$ and then was heated to 50 °C above the expected $T_g$ at a heating rate of 5 °C/min. $T_g$ (the mid-point) was calculated using the computer program within the DSC system. These experiments were also run in duplicate for each sample with the same molecular weight and water content. The final results are an average of the two runs.

## Results and Discussion

*The glass transition in maltodextrin*

*Spin-spin relaxation times ($T_{2S}$).* **Figure 1** shows the $T_{2S}$ vs. temperature curves for maltodextrin DE15 at different water contents. All these curves are characterized by a mirrored 'L' shape. That is, when the temperatures are below a certain point, $T_{2S}$ is almost constant or increases very slowly with increasing temperatures and the average increasing rate of $T_{2S}$ is 0.0113 μs/°C; When the temperatures pass a certain temperature point, $T_{2S}$ increases more rapidly with an average increasing rate of 0.0903 μs/°C, or about nine times

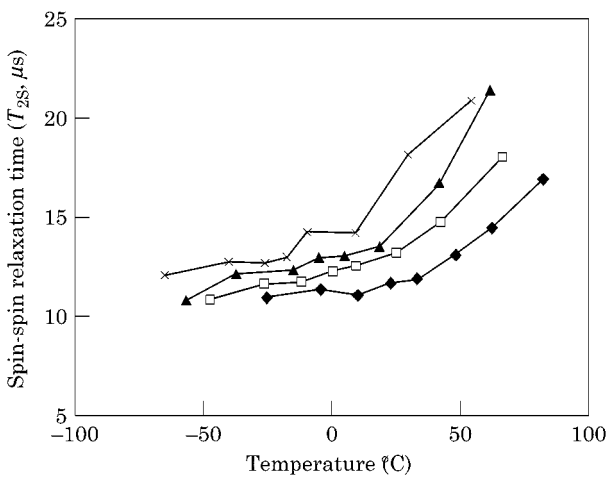


**Fig. 1** The relationship between temperature and $T_{2S}$ in DE15 at different water contents (the legends indicate the water content, g/kg, dry base). (—◆—) = 91 g/kg; (—□—) = 120 g/kg; (—▲—) = 147 g/kg; (—×—) = 183 g/kg

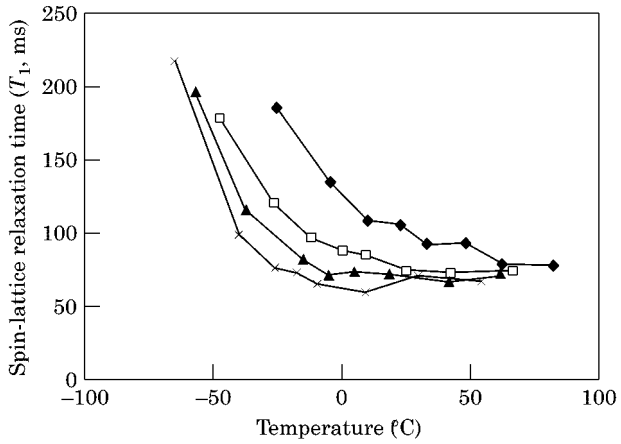


**Fig. 2** The relationship between temperature and spin-lattice relaxation time ($T_1$) in DE15 at different water contents (the legends indicate the water content in g/kg). (—◆—) = 91 g/kg; (—□—) = 120 g/kg; (—▲—) = 147 g/kg; (—×—) = 183 g/kg

higher. This particular temperature point was called the 'turning point' in the $T_{2S}$-temperature curve and marked as $T_{T2S}$.

*Spin-lattice relaxation time ($T_1$).* **Figure 2** shows the $T_1$ vs. temperature curves of DE15 at different water contents. Unlike $T_{2S}$, $T_1$ behaves in an opposite and more complex way. The $T_1$-temperature curves are characterized by an L shape. When the temperature is below a certain point (also called the turning point), $T_1$ decreases with increasing temperatures with an average rate of decrease of −2.373 ms/°C. After passing this turning point, $T_1$ is almost constant or increases and the average rate of change is 0.105 ms/°C, about one twentieth of the rate when the temperatures are below the turning point. The turning point in $T_1$-temperature curves is marked as $T_{T1}$.

*Temperature dependence of $T_{2S}$ and $T_1$ and segmental motions.* Changes in $T_{2S}$ affected by temperature are generally associated with the thermal motion of the molecules. In the glassy state, the material lost its capacity to undergo segmental motion or the segmental mobility of the material was very small (1), and could be treated as a 'solid'. However, when the material enters the rubbery state (above its $T_g$), such motion is intensified due to the increased molecular mobility of the pendants and segments of the molecules. Thus, after passing the transition temperature, the mobility of protons, which are connected with the carbons in the pendants and segments, increases dramatically with temperature, indicated by a much steeper slope on the $T_{2S}$-temperature curves.

Conversely, below the turning point ($T_{T1}$), the decrease in $T_1$ with increasing temperatures is probably also due to the material being in the glassy state. Since there is little segmental motion or molecular mobility in the glassy state, most of the proton rotation occurs at a frequency much lower than the resonance frequency, and requires a much longer correlation time. The num-

ber of protons rotating at the resonance frequency is small so the dynamic contribution to the $T_1$ relaxation process is very small, or the spin energy releasing to the lattice to achieve equilibrium takes a long time. In summary, the spin-lattice relaxation became inefficient in the glassy state-characterized by a very long spin-lattice relaxation time (12, 13). As the temperature increases and approaches $T_{T1}$, $T_1$ gradually decreases due to the increasing number of protons rotating at the resonance frequency. As temperature goes above the $T_{T1}$, the material enters the rubbery state and the structure is transformed from rigid to soft becoming more flexible. After entering the rubbery state, $T_1$ was expected to increase with temperature because it mainly depended on the thermal motion of the molecules in the rubbery state. The significant increases in $T_1$ as the temperature increased was not observed here, probably due to the broad transition range of $T_1$ in DE15 and the limited temperature range used in the investigations.

The turning points on the L or mirrored L shape of $T_{2S}$- or $T_1$-temperature curves were determined using a bilinear regression computer routine. The temperature corresponding to the point where the two lines meet was taken as the turning point.

There is concern about the effect of magnetic resonance frequency on the behavior of $T_1$. A test on the $T_1$ of maltodextrin DE 15 (at 147 g/kg water content) as a function of temperature and frequency (20 MHz and 200 MHz) indicated that the $T_1$ shifted slightly as the magnetic resonance frequency changed but the effect of magnetic resonance frequency on $T_1$ was much smaller than this due to the composition and the glass transition. Despite the large difference in magnetic resonance frequency (about 10 times), the difference in $T_{T1}$ between the two magnetic resonance frequencies is about 20 °C, which is within the error margin of many conventional methods when used in the determination of $T_g$ of food polymers.

**Figure 3** shows $T_g$ from DSC, $T_{T2S}$ and $T_{T1}$ from NMR as a function of the water content. It can be observed that: (1) the $T_{T2S}$ values are very close to the glass transition temperature determined by DSC with the differences between $T_{T2S}$ and $T_g$ being within ±6 °C. $T_{T2S}$ is, on average, 1.2 °C lower than $T_g$; (2) $T_{T1s}$ are also close to but slightly lower than the glass transition temperature determined by DSC. $T_{T1}$ is 11.2 °C lower than $T_g$ on average; and (3) $T_{T1}$ is 10.0 °C above of $T_{T2S}$, on average.

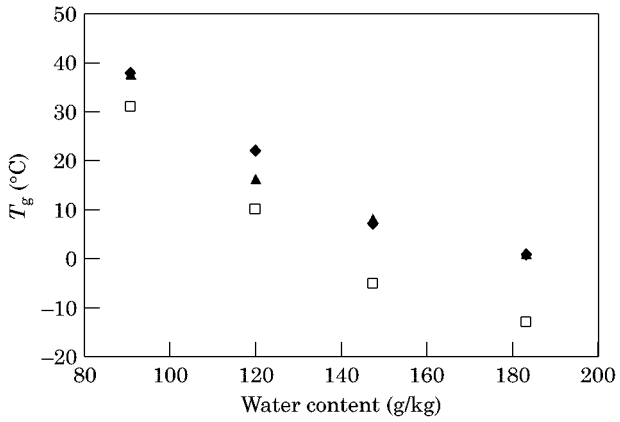


**Fig. 3** Summary of $T_{T2S}$, $T_{T1}$ and $T_g$ in DE15. (♦) = DSC; (□) = $T_1$; (▲) = $T_2$

Due to the plasticization effect of water, the glass transition temperature will decrease with increasing water content in the system. The Gordon-Taylor equation (Eqn [1]) can be used to predict the glass transition temperature ($T_{g,\,predicted}$) in a mixture of two components (polymer and water).

$$T_{g,\,predicted} = \frac{w_1 T_{g_1} + k w_2 T_{g_2}}{w_1 + k w_2} \qquad \text{Eqn (1)}$$

where $w_1$ and $w_2$ are the weight fractions of the polymer and water, $k$ is a constant, $T_{g1}$ and $T_{g2}$ are the glass transition temperatures of the pure polymer and water (K). The glass transition temperature of water is −134 °C (14). The glass transition temperature of the pure polymer is generally very high. For example, $T_g$ of anhydrous gliadin is 121.4 °C (14). According to Eqn [2] $T_{g,\,predicted}$ is greater than $T_g$ of water but less than the $T_g$ of pure polymer and, with an increase in water, the glass transition temperature will decrease. **Figure 3** illustrates that the effects of water on the turning points are similar to those on the $T_g$, that is with an increase in water content, both $T_{T2S}$ and $T_{T1}$ decrease. In summary, the turning points measured by the spin-spin relaxation time and spin-lattice relaxation time are close to the $T_g$ values, and the effect of water on the turning point is similar to that on $T_g$. This strongly suggests that the mobility transition accompanies the glass transition and that the turning points can be used as a measurement of $T_g$.

*The glass transition in bread, cake and cracker*

Because it is difficult to obtain $T_g$ of the real food samples using DSC in this study, we could not evaluate the NMR results using our own DSC data. The $T_g$ data of bread and cracker are available in the literature. However, no $T_g$ data on cake can be found in the literature.

*Bread.* The spin-spin relaxation times ($T_{2S}$) and the spin-lattice relaxation times ($T_1$) of bread samples from the duplicate NMR experiments are shown in **Fig. 4** and **Fig. 5**. The $T_{2S}$-temperature curves are a mirrored L shape, which is same as in maltodextrin samples. Using the bilinear regression program to fit $T_{2S}$-temperature data, the turning points ($T_{T2S}$) for the two runs are −16 °C and −14.3 °C, respectively. The average value is −15.2 °C. The $T_1$-temperature curves are a 'U' shape which is different from the mirrored L shape in the maltodextrin and this is due to the higher water content and molecular weight of the bread sample compared to the maltodextrin samples. In the U shape, the minimum point in the $T_1$-temperature curve was used as the turning point. The turning points ($T_{T1}$) for

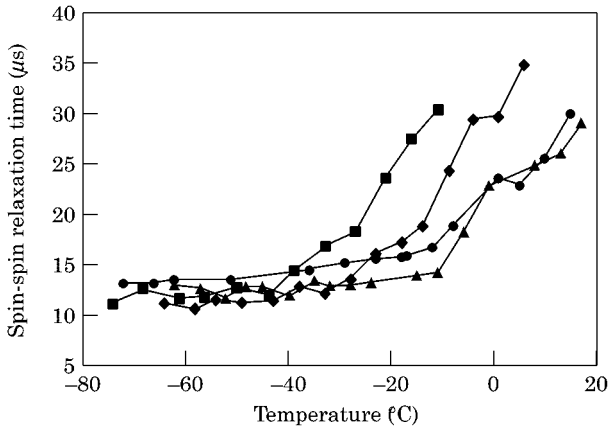


**Fig. 4** The relationship between temperature and $T_{2S}$ in bread and cake (water content, bread 395 g/kg; cake 414 g/kg, wet base). (—♦—) = cake run 1; (—■—) = cake run 2; (—▲—) = bread run 1; (—●—) = bread run 2

both runs are −26 °C and −24.3 °C, respectively. The average value is −25.2 °C. LeMeste *et al.* (15) found that the $T_g$ of white bread with a 37.4% water content was about −12 °C using thermal mechanical analysis (TMA). This is close to $T_{T2S}$ (−15.2 °C) and $T_{T1}$ (−25.2 °C) determined using the NMR relaxation time constants.

*Cake.* The water content of the cake sample is 414 g/g (wet base). The spin-spin relaxation times ($T_{T2S}$) and the spin-lattice relaxation times ($T_1$) of the cake samples from the duplicate NMR experiments are also shown in **Fig. 4** and **Fig. 5**. The $T_{2S}$- and $T_1$-temperature curves are similar to those of the bread sample. The average turning points ($T_{T2S}$) is −27.0 °C (−26.5 °C and −27.4 °C for the two runs, respectively). The $T_{T1}$ values for both runs are −18.7 °C and −23.4 °C, respectively. The average result is −21.1 °C and is 5.9 °C higher than $T_{T2S}$. Thus, the glass transition temperature for the cake sample is about −24 °C.

*Cracker.* The spin-spin relaxation and spin-lattice

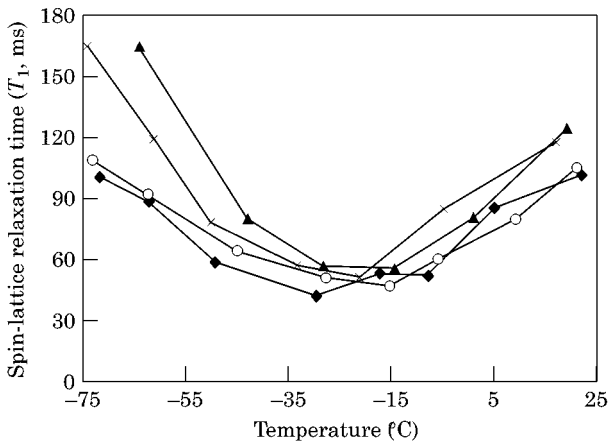


**Fig. 5** The relationship between temperature and $T_1$ in bread and cake (water content, bread 395 g/kg; cake 414 g/kg, wet base). (—♦—) = bread; (—○—) = bread; (—▲—) = cake; (×) = cake

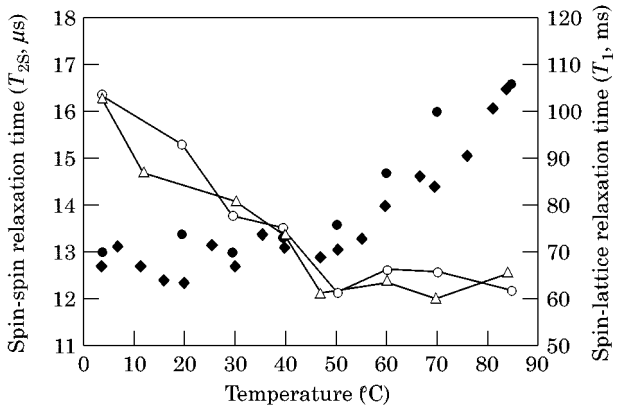


**Fig. 6** The spin-spin and the spin-lattice relaxation times of the cracker sample. (●) = $T_{2S}$, run 1; (♦) = $T_{2S}$, run 2; (—○—) = $T_1$, run 1; (—△—) = $T_1$, run 2

relaxation times of the cracker sample are shown in **Fig. 6**. The $T_{2S}$-temperature curves are also a mirrored L shape. The $T_1$-temperature curves are L shape. The $T_{T2S}$ values are 46 °C and 52.5 °C for the two runs, respectively, with the average being 49.3 °C. The $T_{T1}$ values for both runs are 46.5 and 49.8 °C, respectively, and the average is 48.2 °C. The turning points determined from the spin-spin relaxation and spin-lattice time data are only several degrees different from the $T_g$ value (47 °C) determined by DMTA (16).

However, the bread, cake and cracker used in this study are complicated food systems that contain a wide range of other components which may interfere with our NMR measurement. For example, protons in lipids and proteins may contribute to the nuclear relaxation process. Nevertheless, the trend that relaxation rates changed dramatically under certain thermal conditions is obvious. More investigations employing tightly controlled food systems by the low field NMR is needed to improve our understanding of the relationships between the nuclear relaxation process and the glass transition process in food systems.

## Conclusions

Maltodextrin (DE15), bread, cake and cracker samples were tested using the low field NMR analyzer at temperatures ranging within ±50 °C of the expected glass transition temperature of the samples. The maltodextrin samples were also tested using DSC. It was found that the NMR relaxation times experienced dramatic changes above or below certain temperatures, which were characteristic of the type of material and water content level. The results from the maltodextrin samples, which were used as models, indicate that the characteristic temperatures or turning points determined by using the NMR were very close to the $T_g$ values determined using DSC. It can therefore be concluded that the low field NMR technique provides a useful tool for the analysis of the glass transition process and determination of the glass transition temperature in food polymers.

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