

# A DSC Study on the Gel–Sol Transition of a Starch and Hsian-tsao Leaf Gum Mixed System

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Differential scanning calorimetric analysis was performed on the admixture of 4% hsian-tsao leaf gum and 8% wheat starch as a function of salt types and concentrations. The salt concentrations ( $C_s$ ) studied were 5–100 mM for sodium and potassium chloride, and 3.4–34 mM for calcium and magnesium chloride. It was found that hsian-tsao leaf gum or starch alone did not present a readily recognizable exothermic peak or endothermic peak during cooling or heating in DSC. However, mixing these two polymers promoted the intermolecular binding and subsequent gelation of the mixtures as evidenced by the DSC exothermic and endothermic peaks during cooling and heating, respectively. The setting and melting temperatures of such a mixed system shifted progressively to higher temperatures with increasing concentrations of added salts. It was considered that the aggregated mixed polymers formed thermally stable junction zones with higher binding energies. The thermal behavior change was more remarkable by the addition of  $K^+$  than by  $Na^+$ , and by  $Ca^{2+}$  than by  $Mg^{2+}$ . For monovalent cations, the DSC heating and cooling curves showed a single endothermic and exothermic peak. For divalent cations at low concentration, the DSC curves showed a single peak. However, with sufficient divalent cations, the DSC curves eventually developed a bimodal character. A mixed system with sufficient  $Ca^{2+}$  could form firm gel that was difficult to remelt completely upon heating to 130 °C, indicating the possibility of the formation of ionic bonds through cross-links with the carboxyl groups in hsian-tsao leaf gum.

**Keywords:** *Hsian-tsao gum; starch; mixed system; salts; gel-sol transition*

## INTRODUCTION

Hsian-tsao (*Mesona procumbens* Hemsl) is one of the edible plants containing polysaccharide gum. The unique aroma and several health benefits of hsian-tsao, such as lowering blood pressure and diuretic effect, made it quite popular in the area of Taiwan and south China (Chen et al., 1996). Generally, sodium bicarbonate or sodium carbonate was used to extract the polysaccharide gum in hsian-tsao (Lii and Chen, 1980; Tung, 1998; Fang, 1998; Chao and Lai, 1999a–c; Liu, 1999). The polysaccharide gum can be further isolated from the extract using ethanol (Yang et al., 1982; Chao and Lai, 1999a–c). Compared with other commercial gums, hsian-tsao gum formed a low-viscosity solution with a pronounced shear thinning characteristic (Tung, 1998). Using high performance liquid chromatography, Yang and Huang (1990) found the sugar components of hsian-tsao leaf gum to be galactose, glucose, rhamnose, arabinose, xylose, fructose, mannose, and high levels of uronic acid. Due to its ionic nature, the rheological properties of hsian-tsao leaf gum were found to be strongly affected by ionic strength (Tung, 1998; Chao and Lai, 1999a–c; Lai et al., 2000).

Starch is one of the cheapest polysaccharides and has been found to have widespread applications in the food industry. But starches alone show limitations to achieve adequate viscosity at low concentrations, and they tend to mask flavors and impact an undesirable starchy

texture and taste at higher concentrations (Sudhakar et al., 1996). In addition, they may have very limited ability to control syneresis, which results in water separation in frozen foods during thawing and preparation (Sudhakar et al., 1996; Ferrero et al., 1994). It is well-known that addition of hydrocolloids may increase the viscosity of starch dispersions, influence the retrogradation rate, and prevent syneresis of starch (Liu and Eskin, 1998; Kulicke et al., 1996; Yoshimura et al., 1996, 1998, 1999; Sudhakar et al., 1996; Eidam and Kulicke, 1995; Annable et al., 1994; Alloncle and Doublier, 1991; Alloncle et al., 1989; Christianson, 1982; Christianson et al., 1981). Hsian-tsao gum was also reported to interact with starch synergistically, which resulted in a marked increase in viscosity and the formation of a thermo-reversible gel (Chao and Lai, 1999a). It is generally accepted that the added hydrocolloids result in a modification on the rheological properties of the starch system by influencing amylose gelation (Kulicke et al., 1996; Eidam and Kulicke, 1995; Alloncle and Doublier, 1991; Alloncle et al., 1989).

Ions have been reported to play a fundamental role in the gelation and/or melting mechanism of several polysaccharide polyelectrolytes, such as alginate, pectate, gum arabic, and gellan gum (Lapasin and Priel, 1995; Annable et al., 1994; Miyoshi et al., 1994; 1995; 1996). Though the exact nature of salt–starch interaction is still unclear, Chinachoti et al. (1991) used sodium-23 NMR to show that when starch was gelatinized, the mobility of sodium ions decreased because of salt–starch interaction. Bircan and Barringer (1998) also reported that when salt was added to a starch

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**Table 1. Compositions of Hsian-tsao Leaf Gum<sup>a</sup>**

	proximate compositions (%)				NFE <sup>b</sup>	metal ions (mg/g)				uronic acid (%)
	crude fat	crude protein	ash	crude fiber		Na	K	Ca	Mg	
Hsian-tsao leaf gum	0.52 (0.01)	10.04 (0.21)	26.20 (0.16)	1.47 (0.11)	61.77	61.91 (0.39)	17.74 (0.23)	9.23 (0.16)	16.21 (0.21)	19.87 (0.08)

<sup>a</sup> Each data was expressed as the mean of three replications (standard deviation in parentheses) on a dry basis. <sup>b</sup> Nitrogen-free extracts = 100 - (crude fat + crude protein + ash + crude fiber).

solution, the dielectric loss factor decreased possibly due to the salt–starch interaction that limited salt mobility in response to an electromagnetic field. Annable et al. (1994) reported that the presence of electrolyte could lower the threshold concentration required for phase separation in a maltodextrin/gum arabic mixed system, indicating that starch/charged polysaccharide interaction was strongly affected by the presence of electrolyte. Hsian-tsao leaf gum is considered as a polysaccharide polyelectrolyte due to its high uronic acid content (Yang and Huang, 1990; Chao and Lai, 1999a–c; Lai et al., 2000). The temperature domains of sol–gel and gel–sol transitions of the starch/hsian-tsao leaf gum mixed system may be affected by the presence of salts and are critical to the application of hsian-tsao gum as a food gum. Therefore, the objective of this research was to examine the effects of salt types and concentrations on the sol–gel and gel–sol transitions of the starch/hsian-tsao leaf gum mixed system through differential scanning calorimetry studies.

#### MATERIALS AND METHODS

**Materials.** The dried hsian-tsao leaves were purchased from the farm market, washed with tap water, rinsed with distilled water, and then room-air-dried (25 °C, 48 h). Food grade wheat starch samples, with a total starch content greater than 99%, were kindly supplied by Ku-Tung Inc., Taiwan.

**Extraction of Polysaccharide Gum.** The moisture content of hsian-tsao leaves was determined prior to polysaccharide gum extraction using the method of AOAC (No. 24.003) (1984). Extraction of polysaccharide gum from hsian-tsao herb was performed using the method of Chao and Lai (1999a). Hsian-tsao leaves (4% dry matter) in a sodium bicarbonate solution (0.14 M) were refluxed at 95 °C for 4 h. Hsian-tsao leaf residues were then separated from the polysaccharide extract using a series of sieves (50, 100, 250, and 400 mesh), and a Spectra/Mesh Nylon filter (20 µm). The polysaccharide gum in the extract was then precipitated with 70% ethanol, centrifuged (2000g, 20 min), vacuum-dried (40 °C, 48 h), pulverized, sieved (100 mesh), sealed in zip plastic bags, and then kept in the desiccator for future analysis.

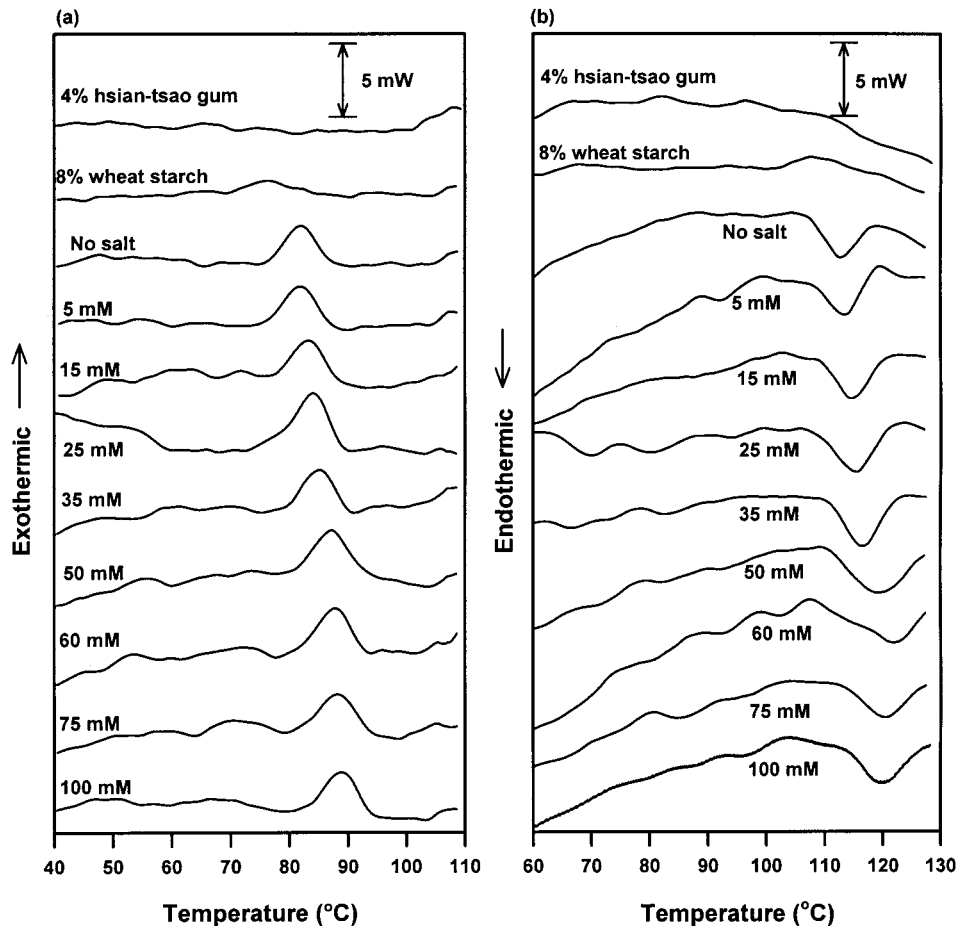
**Compositions of Hsian-tsao Leaf Gum.** The proximate compositions of hsian-tsao leaf gum were analyzed using the methods of AOAC (1984). Uronic acid content was analyzed using the modified carbazole assay (Bitter and Muir, 1962). Sodium, potassium, calcium, and magnesium contents were analyzed using the atomic absorption spectrum method (AOAC, 1984). Results were summarized in Table 1.

**Differential Scanning Calorimetry Analysis.** The sol–gel and gel–sol transitions of the starch/hsian-tsao leaf gum mixed systems were measured using a modulated differential scanning calorimeter (Modulated DSC 2910, TA Instrument, ). Samples were prepared by mixing 8% wheat starch and 4% hsian-tsao leaf gum with deionized water or salt solutions (5–100 mM for sodium and potassium chloride, and 3.4–34 mM for calcium and magnesium chloride) to make the total sample size of 15 ± 0.5 mg. Each sample was hermetically sealed into the DSC sample pan. The empty pan was used as the reference. The sample and reference pans were then placed inside the calorimeter and kept at 140 °C for 10 min. The temperature was lowered from 140 °C to 5 °C at 5 °C/min with

a temperature modulation of 1 °C/min. Samples were then kept at 5 °C for 10 min and raised again at the same rate up to 140 °C. All measurements were performed in at least triplicate.

#### RESULTS AND DISCUSSION

**Effects of Monovalent Cations.** Figure 1 shows the cooling and heating DSC curves of the starch/hsian-tsao leaf gum mixed system with and without sodium chloride. It can be seen that the DSC curves for hsian-tsao leaf gum alone or starch alone did not show recognizable peaks during cooling or heating. However, when mixing hsian-tsao leaf gum and starch together, the cooling curve for the mixed system without salt showed a single exothermic peak at 82.2 °C with an enthalpy value of 0.1956 J/g, and the heating curve showed a single endothermic peak at 112.8 °C with an enthalpy value of 0.1849 J/g. It is generally recognized that an endothermic peak in DSC appears when the system changes from the ordered state to the disordered state, such as the melting of crystals, the transition from gel to sol, the gelatinization of starch, or the denaturation of protein, while an exothermic peak in DSC appears when the system changes from the disordered state to the ordered state such as crystallization or gel formation or retrogradation of starch (Nishinari, 1997). On the basis of the thermal scanning rheological results, Chao and Lai (1999a) reported that hsian-tsao leaf gum could interact with starch synergistically, which resulted in a marked increase in the viscosity of the mixed polymer system. Therefore, the appearance of a single exothermic and endothermic peak for the mixed system implied the formation of a mixed gel during cooling, and the dissolution of the resulting mixed gel during heating of the mixed system. Thermo-reversible (physical) gels are generally formed under conditions that cause extensive formation of polymer–polymer contacts (Braudo and Plashchina, 1995). Such effects resulted from at least two phenomena. First, there were interactions between the solubilized starch (mainly amylose) and the other polysaccharide, such as hsian-tsao leaf gum in this case. Second, the added hydrocolloid (hsian-tsao leaf gum in this case) may compete with starch granules in water, thus affecting the breakdown of starch granules and the amount of solubilized starch (Christianson, 1982; Eidam and Kulicke, 1995). It has also been widely accepted that most thermo-reversible gels consist of somewhat crystalline regions, called junction zones, and somewhat amorphous regions (Moritaka et al., 1992). Mixing hsian-tsao leaf gum and starch seemed to promote the intermolecular binding and subsequent gelation of the mixtures. The junction zones in such mixed gels could be considered as the new ordered structure. The facts that the endothermic peak temperature in the heating DSC curve was higher than the exothermic peak in the cooling DSC curve was called thermal hysteresis and was commonly observed for many thermo-reversible systems (Miyoshi et al., 1994; 1995). Since the sample size used in DSC was very small



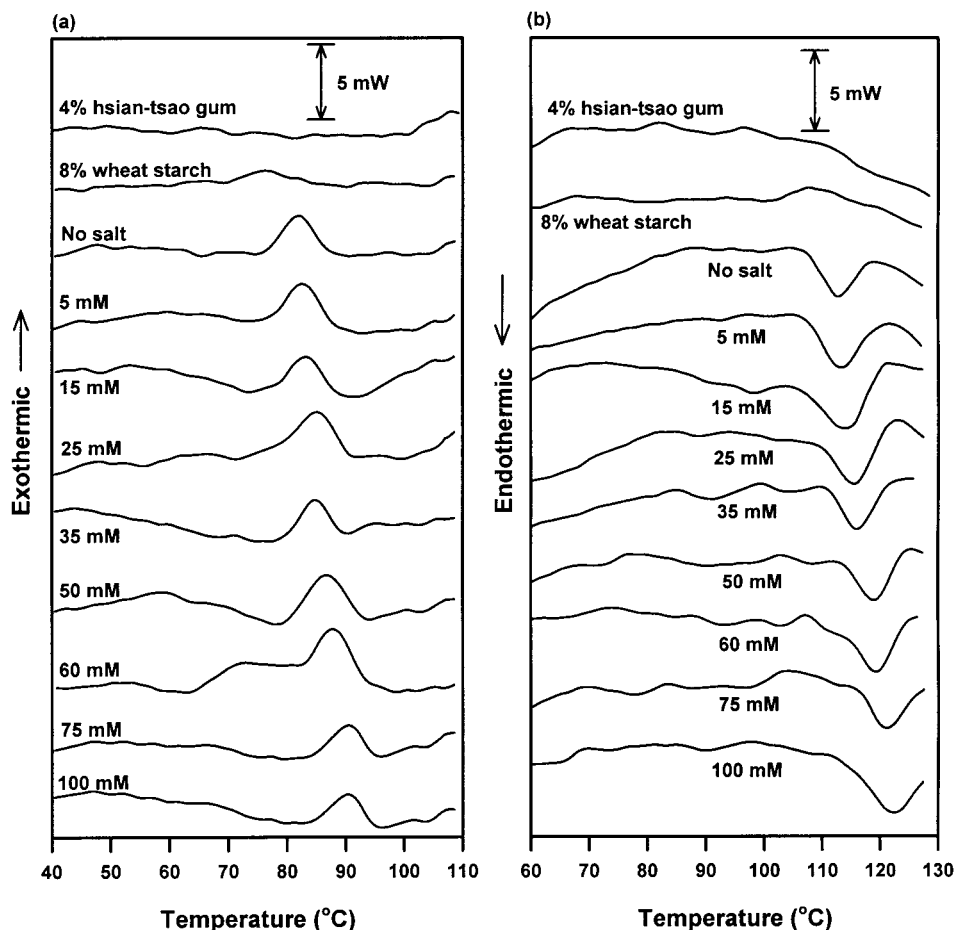
**Figure 1.** Cooling (a) and heating (b) DSC curves for hsian-tsao leaf gum and wheat starch mixtures containing various concentrations of NaCl. Cooling and heating rate = 5 °C/min.

(about 15 mg), the delay in the mass and heat transfer within the mixed system should not be the major reason for pronounced thermal hysteresis. Therefore, it was considered that thermal hysteresis was due to the new ordered structure formed in the mixed system by thermally stable junction zones with significantly high bonding energies.

Figure 1 also clearly demonstrated that both setting and melting temperature shifted to higher temperatures with increasing concentrations of sodium chloride. On the basis of a thermal scanning rheological study, Chao and Lai (1999a) also found that the gel temperature, gel time, and gel viscosity of the starch/hsian-tsao leaf gum mixed system were strongly affected by the presence of ions, possibly due to the ionic nature of hsian-tsao leaf gum. The fact that sodium chloride shifted the exothermic and endothermic peaks to higher temperatures should be attributed to one or a couple of the following possibilities. First, the sodium chloride immobilized water molecules and the effective water content in the mixed gel decreased with increasing sodium chloride concentrations, so that the effective concentrations of starch/hsian-tsao leaf gum increased. Second, the electrostatic shield of anionic groups (carboxylic groups) in hsian-tsao leaf gum molecules by the cations in salt promoted the tight binding and aggregation of the mixed polymers. Third, the sodium chloride molecules interacted directly with starch and/or hsian-tsao leaf gum molecules and promoted the formation and aggregation of molecular chains for the network formation. Nishinari et al. (1990) proposed a zipper model approach to understand the thermo-reversible

gel-sol transition. According to that approach, a gel is assumed to consist of zippers and each single zipper consists of  $N$  parallel links that are secondary weak bonds such as hydrogen bonds. The melting of gels can be simulated as an opening process of molecular zippers from both ends. The addition of sodium chloride may increase the number and the thermal stability of the junction zones in the starch/hsian-tsao leaf gum mixed system.

Figure 2 shows the cooling and heating DSC curves of the starch/hsian-tsao leaf gum mixed system containing various concentrations of potassium chloride. In the case of added potassium chloride, the cooling and heating DSC curves for the mixed system showed a similar tendency to those with sodium chloride. As was seen in this figure, the DSC cooling curves showed a single exothermic peak in all cases, and the setting temperature shifted progressively to higher temperatures with increasing concentrations of added potassium chloride. The DSC heating curves also showed a single endothermic peak in all cases, and the melting temperature shifted progressively to higher temperatures with increasing concentrations of added potassium chloride. It was thought that the presence of cations could shield the electrostatic repulsion of the carboxyl group in hsian-tsao leaf gum and thereby permit tight binding and aggregation of the mixed polymers. However, the influence of potassium chloride on the thermal behavior of the mixed system was more pronounced than that of sodium chloride, as evidenced by a higher setting or melting temperature than a mixed system containing sodium chloride of the same concentration. For example,

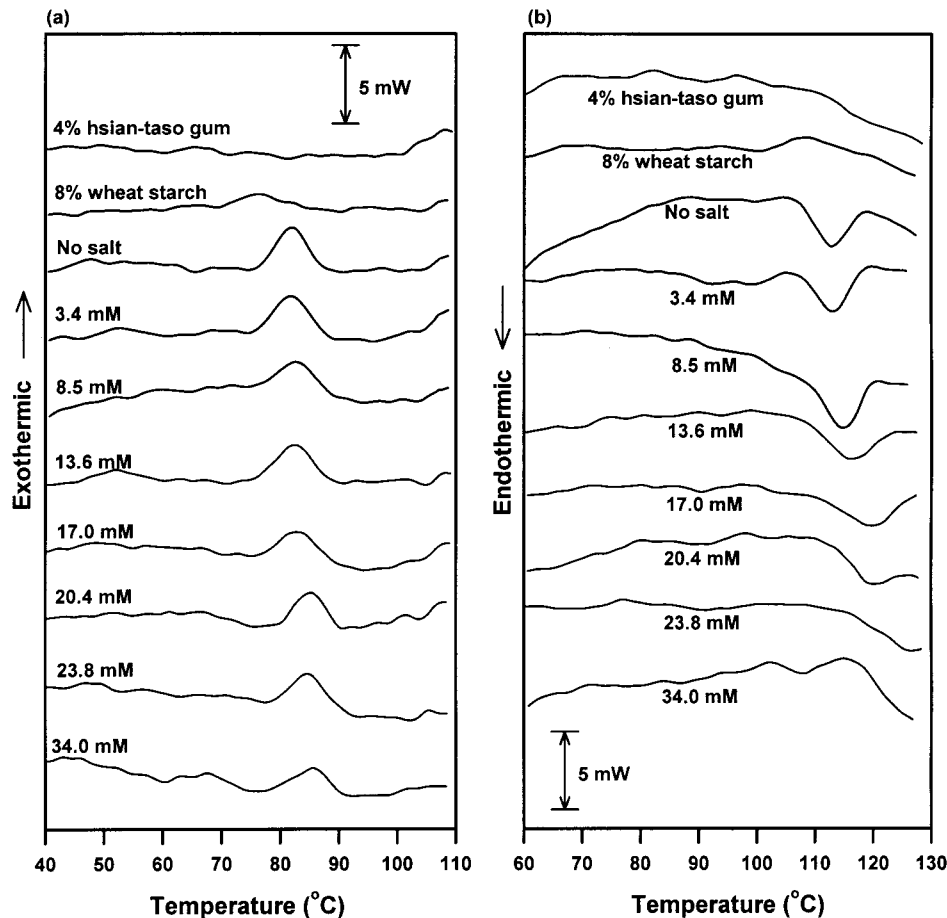


**Figure 2.** Cooling (a) and heating (b) DSC curves for hsian-tsau leaf gum and wheat starch mixtures containing various concentrations of KCl. Cooling and heating rate = 5 °C/min.

the mixed system in the presence of 100 mM of sodium and potassium chloride showed a single exothermic peak on cooling at 89.4 °C with an enthalpy value of 0.2217 J/g and 90.5 °C with an enthalpy value of 0.2110 J/g, respectively, and a single endothermic peak on heating at 120.7 °C with an enthalpy value of 0.2132 J/g and 122.3 °C with an enthalpy value of 0.2058 J/g, respectively. This could be explained by the differences in these two ions in terms of their solvation number or hydration enthalpy and entropy. Since the potassium ion had a lower solvation number and hydration enthalpy but higher hydration entropy than the sodium ion (Hinton and Amis, 1971; Sawayama and Kawabata, 1991), it could be considered as a structure-disordering ion while sodium ion was the structure-ordering ions (Miyoshi et al., 1994). This structure-disordering feature of potassium ion facilitated the tight binding and aggregation of the mixed polymer.

**Effects of Divalent Cations.** Figure 3 shows the cooling and heating DSC curves of the hsian-tsau leaf gum/starch mixed system containing various concentrations of calcium chloride. The behavior of the mixed system with calcium chloride was different from that with monovalent cations. Although the setting temperature shifted to higher temperatures with increasing concentrations of calcium chloride, the DSC cooling curves only showed a single exothermic peak at a lower calcium chloride concentration, but eventually developed a bimodal character with progressive addition of calcium chloride. As shown in Figure 3, with the addition of 3.4 mM calcium chloride, the cooling DSC showed only one exothermic peak at 82.8 °C with an

enthalpy value of 0.2078 J/g. However, with the addition of 34 mM calcium chloride, the cooling DSC curve showed a main exothermic peak at 86.5 °C with an enthalpy value of 0.1411 J/g and a second exothermic peak at 67.4 °C with an enthalpy value of 0.0749 J/g. In terms of a zipper model approach, the appearance of two exothermic peaks in the cooling DSC curve suggested the formation of junction zones with different bonding energies or rotational freedoms. Similarly, although the melting temperature of the mixed system seemed to shift to higher temperature with increasing calcium chloride concentration, the main endothermic peak in the heating DSC curve for the mixed gels containing 34 mM calcium chloride was not found, whereas a minor peak at 108.4 °C with an enthalpy value of 0.0522 J/g was found. It was therefore considered that the starch/hsian-tsau leaf gum mixed system with sufficient calcium chloride could form firm gel on cooling to below the setting temperature and could not be melted completely. It is well-known that the bond energy for ionic bonds or covalent bonds is far higher than that of hydrogen bonds or for hydrophobic interactions. Since the mixed gel in the presence of sufficient  $\text{Ca}^{2+}$  could not be melted completely on heating to 130 °C, the possibility of the formation of ionic bonds by  $\text{Ca}^{2+}$  may not be excluded. In other words, in the starch/hsian-tsau leaf gum mixed system,  $\text{Ca}^{2+}$  could make cross-links with the carboxyl groups of hsian-tsau leaf gum through ionic bonds in addition to charge-screening effects. The thermal hysteresis of the mixed system with higher salts was found to be more pronounced as compared to that observed in the mixed system with



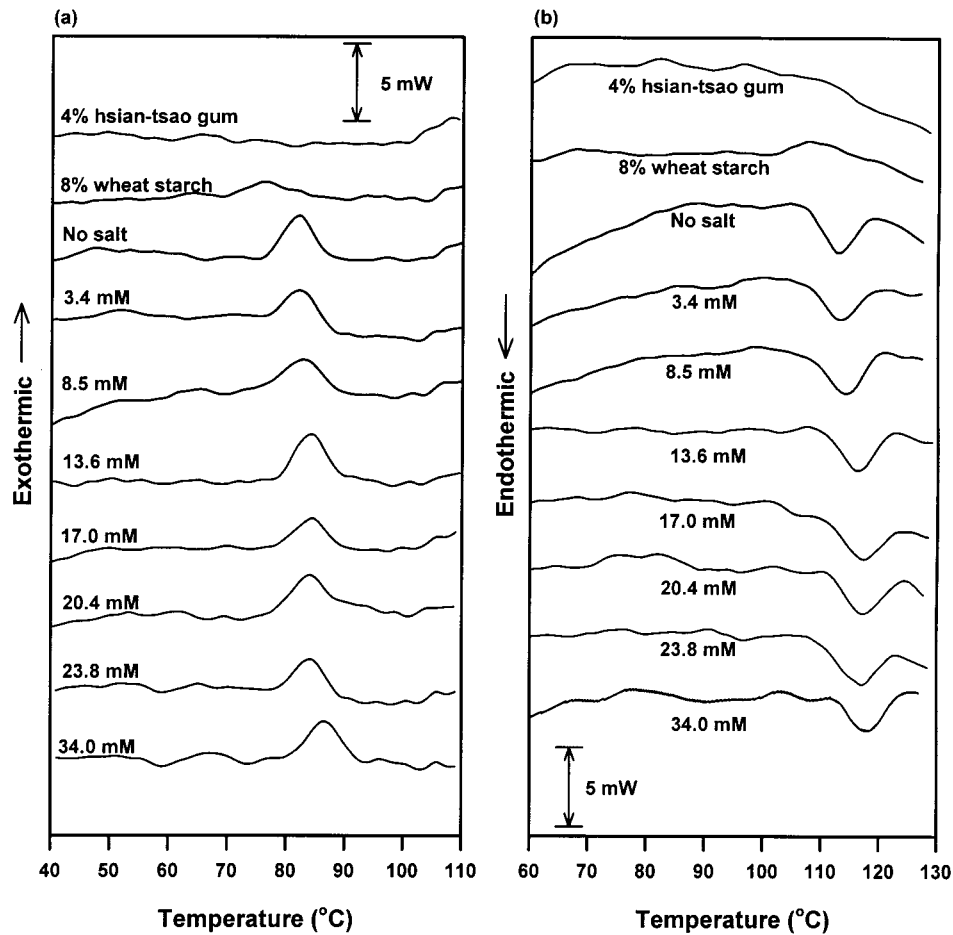
**Figure 3.** Cooling (a) and heating (b) DSC curves for hsian-tso leaf gum and wheat starch mixtures containing various concentrations of  $\text{CaCl}_2$ . Cooling and heating rate =  $5\text{ }^\circ\text{C}/\text{min}$ .

less salt. For example, for the mixed system with 3.4 mM calcium chloride, the setting and melting temperature were  $82.8\text{ }^\circ\text{C}$  with an enthalpy value of  $0.2078\text{ J/g}$  and  $113.1\text{ }^\circ\text{C}$  with an enthalpy value of  $0.2032\text{ J/g}$ , respectively. However, for the mixed system with 20.4 mM calcium chloride, the setting and melting temperature were  $84.1\text{ }^\circ\text{C}$  with an enthalpy value of  $0.2271\text{ J/g}$  and  $120.4\text{ }^\circ\text{C}$  with an enthalpy value of  $0.1712\text{ J/g}$ , respectively. Therefore, it was considered that with increasing concentration of added salt, the aggregation of intermolecular chains was promoted, and the higher temperature peak originated from the aggregated mixed polymers formed by thermally stable junction zones with higher binding energies was observed.

Figure 4 shows the cooling and heating DSC curves of the hsian-tso leaf gum/starch mixed system containing various concentrations of magnesium chloride. The behavior of the mixed system with magnesium chloride was similar to that with calcium chloride. The setting temperature shifted to higher temperatures with increasing concentrations of magnesium chloride and eventually developed a bimodal character with progressive addition of magnesium chloride. As shown in Figure 4, with the addition of 8.5 mM magnesium chloride, the cooling DSC showed only one exothermic peak at  $82.6\text{ }^\circ\text{C}$  with an enthalpy value of  $0.2152\text{ J/g}$ . However, with the addition of 34 mM magnesium chloride, the cooling DSC curve showed a main exothermic peak at  $86.3\text{ }^\circ\text{C}$  with an enthalpy value of  $0.1875\text{ J/g}$  and a second exothermic peak at  $66.8\text{ }^\circ\text{C}$  with an enthalpy value of  $0.0803\text{ J/g}$ . Similarly, the melting temperature shifted to higher temperatures with increasing concentrations

of magnesium chloride and eventually developed a bimodal character with progressive addition of magnesium chloride. As shown in Figure 4, with the addition of 8.5 mM magnesium chloride, the heating DSC showed only one endothermic peak at  $114.8\text{ }^\circ\text{C}$  with an enthalpy value of  $0.196\text{ J/g}$ . However, with the addition of 34 mM magnesium chloride, the heating DSC curve showed a main endothermic peak at  $118.5\text{ }^\circ\text{C}$  with an enthalpy value of  $0.2035\text{ J/g}$  and a second endothermic peak at  $108.1\text{ }^\circ\text{C}$  with an enthalpy value of  $0.0104\text{ J/g}$ . The influence of calcium chloride on the thermal behavior of the mixed system was more pronounced than that of magnesium chloride, as evidenced by a higher setting or melting temperature at relevant concentration. For example, the mixed system in the presence of 23.8 mM divalent cations showed a main exothermic peak on cooling at  $85.4\text{ }^\circ\text{C}$  for  $\text{Ca}^{2+}$  and  $84.9\text{ }^\circ\text{C}$  for  $\text{Mg}^{2+}$ , respectively, and an incomplete main endothermic peak on heating at  $124.8\text{ }^\circ\text{C}$  for  $\text{Ca}^{2+}$  and a complete endothermic peak at  $117\text{ }^\circ\text{C}$  for  $\text{Mg}^{2+}$ , respectively.

As the thermal behavior of the mixed system with monovalent cations was compared to that with divalent cations, it was found that the mixed system with sufficient divalent cations could form firm gel that was difficult to be remelted completely. Since the electric charges of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  are larger than those of  $\text{Na}^+$  or  $\text{K}^+$ ,  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  can shield the electrostatic repulsion of the carboxyl groups in hsian-tso leaf gum more effectively than  $\text{Na}^+$  or  $\text{K}^+$ , as in the case of gellan gum (Miyoshi et al., 1994). The gel-to-sol transition of thermal reversible gels is determined by at least three parameters. First is the bonding energy required for a

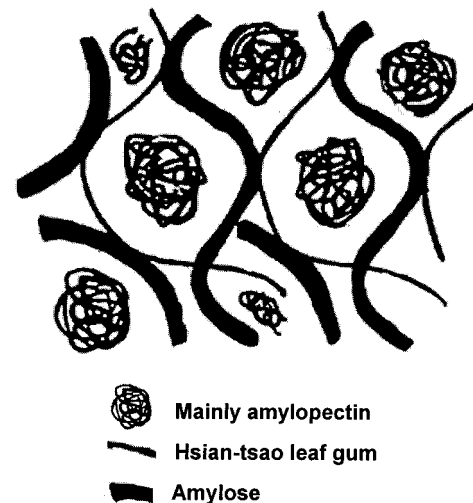


**Figure 4.** Cooling (a) and heating (b) DSC curves for hsian-tsao leaf gum and wheat starch mixtures containing various concentrations of  $MgCl_2$ . Cooling and heating rate =  $5\text{ }^\circ\text{C}/\text{min}$ .

chain segment to be released from a junction zone. Second is the ceiling number that is the number of chain segments liberated from junction zones before gel-to-sol transition could occur. Third is the mean end-to-end distance between junction zones (Miyoshi et al., 1994, 1995, 1996). It was suggested that on addition of cations, both the bonding energy and ceiling number increased, but the mean end-to-end distance decreased by the increase in the number of the junction zones. Therefore, it was also considered that divalent cations (calcium and magnesium chloride in this case) seemed to increase bond energy and ceiling number more effectively than monovalent cations (sodium and potassium chloride in this case). Due to the development of a bimodal character in DSC curves, it is moreover suggested that the network of the mixed system containing divalent cation is formed by junction zones with different thermal stability.

#### CONCLUSION

Within the experimental conditions and concentration range studied, hsian-tsao leaf gum or starch alone did not show readily recognizable exothermic peak or endothermic peak during cooling or heating in DSC. However, mixing these two polymers seemed to promote the intermolecular binding and subsequent gelation of the mixtures as evidenced by the DSC exothermic and endothermic peaks during cooling and heating, respectively. A highly schematic presentation of the structure of the mixed gel is shown in Figure 5. In such a mixed



**Figure 5.** Highly schematic presentation of hsian-tsao leaf gum/starch mixed gel.

system, much of the amylose leached out of the starch granules during heating preparation of the sample, and the amylose and amylopectin had essentially phase separated. The leached out amylose rearranged itself and formed a coupled network with hsian-tsao leaf gum. The setting and melting temperatures of such a mixed system shifted progressively to higher temperatures with increasing concentrations of added salts. It seemed that the introduction of cations to the mixed system increased the number of junction zones and decreased

the rotational freedom of parallel links. Such an operation made the structure of junction zones in the mixed gel more heat resistant.

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