

# Effect of Polarity of Complexing Agents on Thermal and Rheological Properties of Rice Starch Gels

John T. Chien,<sup>1,2</sup> Ya-Yi Lien,<sup>1</sup> and C. F. Shoemaker<sup>3</sup>

## ABSTRACT

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The ability of rice starch to complex with ligands of various polarities was studied to examine the mechanism of complex formation in an aqueous solution. Differential scanning calorimetry (DSC) showed that TNU519 rice starch (27.9% amylose) formed inclusion complexes with all 12-C complexing agents. The onset melting temperatures ( $T_o$ ) of the complexes were  $\approx 93$ – $96^\circ\text{C}$ . The saturation concentrations of added ligands with high polarity, lauric acid (LA), and lauryl alcohol (LOH), had a range of 2–4% (w/w) of the starch, and both of the corresponding melting enthalpies ( $\Delta H$ ) were  $\approx 3.0$  J/g. In contrast, the saturation concentrations of ligands with low polarity, methyl laurate (ML) and dodecane (DO), were  $\approx 1$ – $2\%$  (w/w), and the  $\Delta H$  were 1.87 and 1.80 J/g, respectively. This implied that

solubility of ligands had a significant effect on the extent of complexation. The  $T_o$  and  $\Delta H$  increased with an increase of annealing time at  $85^\circ\text{C}$ , and the optima for the partially reversible complex formation were 2 hr of annealing in all cases. When measured by a dynamic rheometer, the TNU519 rice starch gel with added LA or LOH showed a higher storage modulus ( $G'$ ) than that with no complexing agent added during heating. The  $G'$  and  $\tan \delta$  of the complexed gel were further increased during 12 hr of storage. The increase of  $G'$  indicated that the elastic structure of the concentrated rice starch gels could be improved by complex formation and annealing, whereas the increase of  $\tan \delta$  suggested incompatibility of starch components during storage.

Amylose leached out during gelatinization can form a three-dimensional gel network with the swollen starch granules embedded in the matrix during cooling (Eliasson 1985, Imberty et al 1991). It is generally accepted that both the continuous phase of amylose and the discontinuous phase of swollen granules and gelatinized amylopectin contribute to the gel properties. Starch retrogradation occurring during storage often accompanies a decrease in gel rigidity (Biliaderis and Juliano 1993). This effect is lessened by the presence of lipids (Eliasson and Krog 1985, Eliasson 1986), presumably due to their abilities in complex formation and reduction of granule swelling. It is well known that many added lipids or ligands can, at least under certain circumstances, enter the helical cavities of starch molecules and largely modify the rheology of starch-containing foods (Krog 1973, Biliaderis and Juliano 1993). Amylose, as compared with amylopectin, easily forms crystalline, V-polymorphic complexes with polar and nonpolar organic ligands (Young 1984, Biliaderis 1992). These complexes play an essential role in processes associated with the utilization of starch-containing ingredients. Thus, the texture and gel stability of cereal-based products are greatly influenced by the complex formation of the amylose component and various ligands (Hoover and Hadziyev 1981, Schuster and Adams 1984).

Complexes of amylose with fatty acids or monoglycerides differing in carbon chain length have been well studied (Eliasson and Krog 1985, Hahn and Hood 1987, Raphaelides and Karkalas 1988). Attempts to characterize the complexes of rice starch have been made recently using differential scanning calorimetry (DSC). Such studies revealed a reversible high-temperature transition ( $90$ – $120^\circ\text{C}$ ) that was attributed to the order  $\rightarrow$  disorder transition of the amylose-ligand complex (Hoover and Hadziyev 1981). The aim of this study was to examine the effective complexation of rice starch with added ligands of various polarities. This could provide further insight into the mechanism of amylose-ligand binding. Effects of concentration of ligands and annealing time on the degree of complexation were also investigated through thermal analyses. Dynamic rheometry was used to further evaluate the changes in molecular structure of the complexed rice starch gels during annealing.

## MATERIALS AND METHODS

### Rice Starches

Two kinds of rice starch, indica (Tai-Nung Sen 19, TNU519) and waxy (Tai-Chung Sen Waxy 1, TCSW1) varieties, were isolated from milled rice by a modified alkaline steeping method (Yang et al 1984). To determine the extent of starch complexation with added ligands, the starches were dried at  $40^\circ\text{C}$  and defatted by hot extraction with 85% (v/v) aqueous methanol solution for 24 hr and with 100% methanol for 6 hr according to the method of Schoch (1942). Amylose was determined according to the method of Juliano et al (1981), using potato amylose-waxy rice starch (Tai-Chung Waxy 46 rice starch) standard mixtures. The amounts of protein ( $N \times 6.25$ ) and lipid were analyzed according to the methods of Eliasson et al (1981). Approved Method 08-01 (AACC 1995) was used for ash determination.

### Preparation of Inclusion Complexes

Four complexes of rice starch with lauric acid (LA), lauryl alcohol (LOH), methyl laurate (ML), and dodecane (DO) were prepared. The defatted TNU519 rice starch suspension (33.3%, w/w) was first partially gelatinized at  $85^\circ\text{C}$  and then completely gelatinized at  $110^\circ\text{C}$  for 15 min in a pressure cooker. Complexes were formed under vigorous stirring for 15 min at  $85^\circ\text{C}$  after a Tween-60 emulsion solution was added. The emulsion solution was made by mixing one part hydrogenated palm oil (containing 60%, w/v, of ligand) with two parts aqueous solution (containing 0.7%, w/v, of Tween-60) at  $50^\circ\text{C}$  and homogenizing at 8,000 rpm for 5 min. The complexes were annealed at  $85^\circ\text{C}$  for specified times. Subsequently, they were slowly cooled and held at  $50^\circ\text{C}$  for 30 min, before being further cooled to room temperature to form a gel. The complexed starch gels were then freeze-dried and washed four times with acetone to remove excess free ligand. Finally, the complexes were air-dried in a hood for 24 hr.

### Calorimetry

The thermal properties of the starch and the complexed samples were examined with a differential scanning calorimeter (1090, DuPont, Wilmington, DE) equipped with a 910 DSC pressure cell (500 psi with  $N_2$ ). An aqueous suspension (33.3%, w/w) was used as the sample. Approximately 7.5 mg of sample was hermetically sealed in a coated aluminum pan and equilibrated at room temperature for 24 hr. A sealed empty pan was used as a reference. The sample was first heated from 25 to  $135^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ , held at  $135^\circ\text{C}$  for 30 min, and then cooled to room temperature before

<sup>1</sup> Dept. of Nutrition and Food Sciences, Fu-Jen University, Taipei, Taiwan, R.O.C.  
<sup>2</sup> Corresponding author. E-mail: nutr1000@mails.fju.edu.tw Phone: 886-229-031-111 ext. 3627.  
<sup>3</sup> Department of Food Science and Technology, University of California, Davis, CA 95616.

being rescanned to 135°C at 10°C/min. The melting onset temperature ( $T_o$ ) and enthalpies ( $\Delta H$ ) of the characteristic transitions were recorded (Imeson et al 1977, Biliaderis et al 1985). After the DSC pressure cell was heated to 550°C for cleaning, the instrument was calibrated with indium by heating from 25 to 200°C at 10°C/min and  $\Delta H$  was calculated from the peak area of the thermogram.

### Rheology

The complexed starch gel (15%, w/w) was prepared as previously described, except that the amount of ligand added to the starch was fixed at 4% (w/w), and 2 hr of annealing at 85°C was used for all samples. Formation of gas bubbles in the gel was avoided during mixing, or a subsequent degassing step was done according to the method of Kim et al (1992). Before the rheological test, the gel was carefully sampled with a metal scoop without disturbing the gel structure.

Small amplitude oscillatory rheological tests were conducted using a dynamic rheometer with controlled stress (Carri-Med-CSL<sup>2</sup> 500, TA Instrument Ltd., Surrey, England), equipped with a cone-and-plate system (4 cm dia. and 2° cone angle). The gap distance was fixed at a constant 55  $\mu$ m during heating from 25 to 95°C. The shear strain and frequency were set at 1.0% and 1 Hz, respectively, for all determinations. Effects of complexing agents on the dynamic rheological properties of TNU19 rice starch gels were investigated by measurements of the storage modulus ( $G'$ ), loss modulus ( $G''$ ), dynamic viscosity ( $\eta'$ ), and  $\tan \delta$ . Data are presented as the mean of triplicate measurements. To avoid the evaporation of water during each measurement, a solvent trap filled

with silicon oil (low viscosity) was used, and the sample outside the plate was removed, and the remaining sample on the rim was covered by a thin layer of silicon oil. The starch samples, with or without 12 hr of prior storage at room temperature, were heated from 25 to 95°C at 1.5°C/min during the determinations (Lii et al 1995).

### Statistical Analyses

Analysis of variance and comparisons among treatments were conducted on the thermal data and were computed using the Statistical Analysis System (SAS Institute, Cary, NC). The differences among treatments were determined by Duncan's multiple range test after a preliminary  $F$  test at the 5% probability level.

## RESULTS AND DISCUSSION

### Composition of Rice Starch

The chemical compositions of TNU19 and TCSW1 rice starches and flours are listed in Table I. Both flours contained a small amount of lipids (0.48 and 0.46%, respectively). The presence of internal granular lipids would depress later complex formation of amylose (Mikus et al 1946) and amylopectin (Huang and White 1993) with added ligands. Therefore, the starches were defatted to 0.14 and 0.13%, respectively, before use. The trace amounts of remaining lipids are mainly bound free fatty acids and phospholipids in the rice starch (Kitahara et al 1997). The amylose contents of the TNU19 and TCSW1 rice flours were 25.6 and 1.2% (w/w), respectively. The calculated values in the corresponding rice starches were 27.9 and 1.3% (w/w), respectively.

### Effects of Ligand Polarity and Concentration on Thermal Properties

Four ligands with the same 12-carbon chain length differ with respect to the polarity of their functional groups. The order of polarity is LA>LOH>ML>DO. DSC results showed that TNU19 rice starch formed inclusion complexes with all the ligands. The  $T_o$  of all four complexes was  $\approx$ 93–96°C and was not significantly different. No endothermic peak was found at 80–120°C for the mixture of Tween-60 aqueous solution and the rice starches (data

TABLE I  
Chemical Composition of Rice Starch and Flour<sup>a</sup>

Variety	Starch, %			Flour, %			
	Protein	Lipid	Amylose	Protein	Lipid	Ash	Amylose
TNU19	0.72	0.14	27.9	8.05	0.48	0.39	25.6
TCSW1	0.38	0.13	1.3	6.58	0.46	0.42	1.2

<sup>a</sup> Means of triplicate measurements (% db). Protein (N  $\times$  6.25).

TABLE II  
Thermal Analysis<sup>a,b</sup> of Inclusion Complexes of TNU19 Rice Starch

Concentration (%, w/w)	Lauric Acid		Lauryl Alcohol		Methyl Laurate		Dodecane	
	$T_o$	$\Delta H$	$T_o$	$\Delta H$	$T_o$	$\Delta H$	$T_o$	$\Delta H$
0.2	95.1a	1.23e	94.4a	0.83d	94.7a	0.80d	95.3a	0.68d
0.5	94.4a	1.67d	95.8a	1.68c	95.6a	1.06c	95.0a	1.10c
1	94.7a	2.11c	93.8a	2.22b	94.7a	1.42b	94.4a	1.36b
2	93.6a	2.55b	94.1a	2.51b	94.0a	1.87a	94.5a	1.80a
4	95.0a	3.04a	94.5a	3.00a	94.4a	1.86a	94.7a	1.80a
6	93.3a	3.01a	94.2a	3.00a	94.2a	1.83a	93.7a	1.84a
8	95.4a	2.92a	94.6a	3.01a	94.5a	1.87a	94.1a	1.80a

<sup>a</sup> Onset melting temperatures ( $T_o$ , °C) and melting enthalpies ( $\Delta H$ , J/g).

<sup>b</sup> Values followed by the same letter are not significantly different ( $P < 0.05$ );  $n = 3$ .

TABLE III  
Effect of Annealing Time on Thermal Properties<sup>a,b</sup> of Inclusion Complexes of TNU19 Rice Starch with Polar Ligands

Annealing Time (min)	Lauric Acid					Lauryl Alcohol				
	Heating		Reheating		%	Heating		Reheating		%
	$T_o$	$\Delta H$	$T_o$	$\Delta H$		$T_o$	$\Delta H$	$T_o$	$\Delta H$	
0	95.0c	3.04d	104.2c	2.16d	71.1	94.5c	3.00d	104.0c	1.91d	63.7
30	96.5c	3.76c	105.2c	2.64c	70.2	95.2c	3.70c	105.5c	2.39c	64.6
60	98.4b	4.36b	107.8b	3.49b	80.0	96.9b	4.22b	107.4b	3.30b	78.2
120	101.9a	5.25a	112.1a	4.31a	82.1	100.5a	5.10a	110.4a	4.16a	81.6
300	102.0a	5.29a	112.9a	4.44a	83.9	100.9a	5.16a	111.2a	4.18a	81.0

<sup>a</sup> Onset melting temperatures ( $T_o$ , °C) and melting enthalpies ( $\Delta H$ , J/g); annealing enthalpy (%):  $\Delta H(\text{reheating})/\Delta H(\text{heating})$ .

<sup>b</sup> Values followed by the same letter are not significantly different ( $P < 0.05$ );  $n = 3$ .

not shown). The  $\Delta H$  increased with increasing concentration of each ligand and reached a maximum at the saturation concentration (Table II). This indicated that the thermal stability ( $T_o$ ) of the complex was not significantly different with respect to the percentage and polarity of the added ligand, although its  $\Delta H$  was substantially different. The saturation concentrations of the added ligands with high polarity, LA and LOH, had a range of 2–4% (w/w) of the starch, and the corresponding  $\Delta H$  were 3.04 and 3.00 J/g, respectively. Samples with low-polarity ligands, ML and DO, had saturation concentrations of  $\approx 1$ –2% (w/w), and the  $\Delta H$  were 1.87 and 1.80 J/g, respectively (Table II). These results revealed the fact that ligands with high polarity had a comparatively higher degree of complexation with TNU19 rice starch than did ligands with low polarity. The above findings appear to contradict the results of Krog (1971), which showed that fatty acids with a large polar group were poor amylose complexing agents. Those results were based on evidence that the lipophilic character of the amylose helix has an important effect on the extent of complexation. However, mixing conditions governing the solubility of ligands should also be considered. For a short mixing time, free ligands released from the disrupted emulsion system at 85°C needed to be dissolved in hot water before they could become available to amylose molecules and form complexes. Thus, polar ligands with a higher solubility in hot water could eventually have greater complexing ability with amylose.

In contrast to calorimetric results for maize amylopectin (Eliasson et al 1981), no endothermic peak was found for any of the mixtures of TCSW1 rice starch and the four ligands (data not shown). Although the nature of the amylopectin-lipid complex remains obscure, it is likely that only the longer accessible linear chains (outermost branches) of amylopectin molecules can interact with

lipids (Slade and Levine 1987, Biliaderis and Tonogai 1991). Our results were consistent with the calorimetric studies of Wu et al (1993) on rice starches. Compared with the TNU19 rice starch, the TCSW1 rice starch contained only 1.3% (w/w) amylose and was much less capable of forming complexes with ligands. That amount of complexation, if any, was below the threshold for the DSC measurements made.

### Effect of Annealing on Thermal Properties

Although a crystalline polymer is considered to have a distinct melting point determined by its molecular dimensions, it tends to show increased perfection upon heating (i.e., annealing) at temperatures below the melting point (Wunderlich 1981). The annealing behavior was observed for the TNU19 rice starch complexes. DSC results showed that  $T_o$  and  $\Delta H$  increased with increasing annealing time at 85°C (Tables III and IV). Since no complex was observed between rice amylopectin and added ligands, the annealing behavior was mainly due to realignment of amylose-lipid complexes, which was also evidenced in the studies of Biliaderis et al (1985). Our study showed that the annealing time for optimal complex formation, based on  $T_o$  and  $\Delta H$  after heating, was 2 hr in all cases. An endothermic peak was also observed during the rescanning of each complex (Tables III and IV). Evidently, this was due to the partially reversible complexation between the ligand and the amylose in TNU19 rice starch. It appears that the thermal events seen after the annealing and cooling processes were associated with the organization of the amylose-ligand helices into a more perfect partially crystalline structure. We calculated the change in  $\Delta H$  in terms of the percentage of the annealing enthalpy of each complex:  $\Delta H(\text{reheating})/\Delta H(\text{heating})$ . It was interesting to note that the percentages of reversibility were increased with increasing anneal-

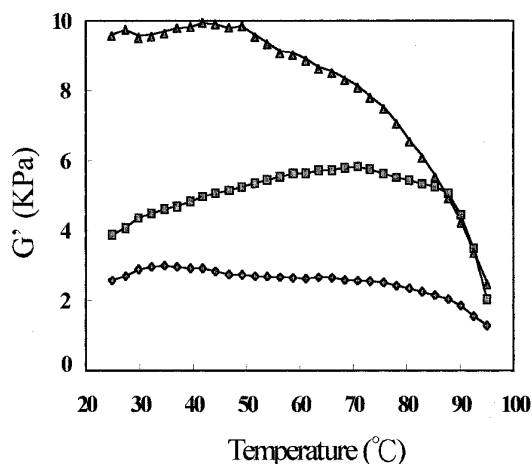


Fig. 1. Effects of lauric acid and storage on storage moduli ( $G'$ ) of TNU19 rice starch gels during heating: gel without lauric acid ( $\blacklozenge$ ), with lauric acid ( $\blacksquare$ ), and after 12 hr of storage ( $\blacktriangle$ ).

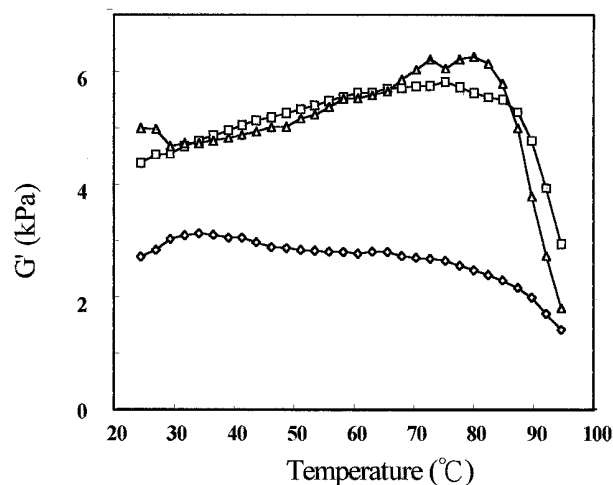


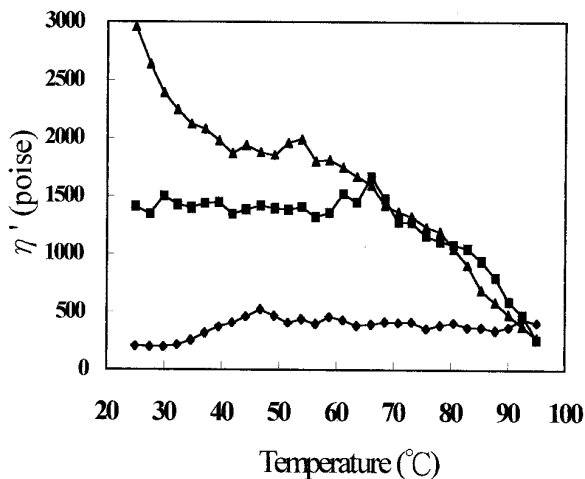
Fig. 2. Effects of lauryl alcohol and storage on storage moduli ( $G'$ ) of TNU19 rice starch gels during heating: gel without lauryl alcohol ( $\diamond$ ), with lauryl alcohol ( $\square$ ), and after 12 hr of storage ( $\triangle$ ).

TABLE IV  
Effect of Annealing Time on Thermal Properties<sup>a,b</sup> of Inclusion Complexes of TNU19 Rice Starch with Nonpolar Ligands

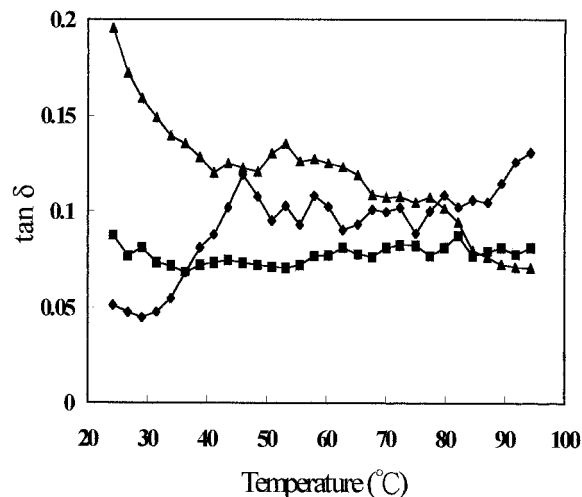
Annealing Time (min)	Methyl Laurate					Dodecane				
	Heating		Reheating			Heating		Reheating		
	$T_o$	$\Delta H$	$T_o$	$\Delta H$	%	$T_o$	$\Delta H$	$T_o$	$\Delta H$	%
0	94.0c	1.87d	102.6c	0.77d	41.2	94.5c	1.80d	102.5d	0.67e	37.2
30	95.3c	2.40c	106.6b	1.30c	54.2	95.3c	2.38c	106.5c	1.23d	51.7
60	97.7b	2.85b	108.2b	1.63b	57.2	98.3b	2.82b	108.2b	1.63c	57.8
120	101.6a	3.23a	111.7a	2.11a	65.3	100.6a	3.01a	110.7a	1.90b	63.1
300	101.7a	3.25a	112.5a	2.17a	66.8	101.7a	3.13a	110.9a	2.08a	66.5

<sup>a</sup> Onset melting temperatures ( $T_o$ , °C) and melting enthalpies ( $\Delta H$ , J/g); annealing enthalpy (%):  $\Delta H(\text{reheating})/\Delta H(\text{heating})$ .

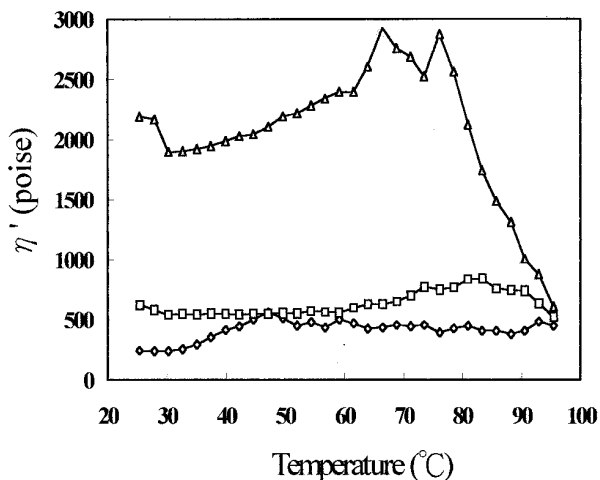
<sup>b</sup> Values followed by the same letter are not significantly different ( $P < 0.05$ );  $n = 3$ .



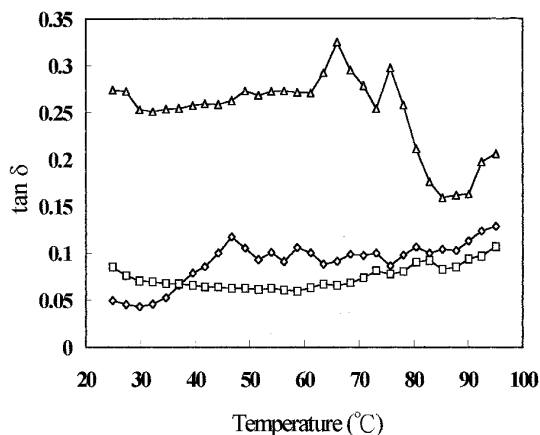
**Fig. 3.** Effects of lauric acid and storage on dynamic viscosity ( $\eta'$ ) of TNuS19 rice starch gels during heating: gel without lauric acid ( $\blacklozenge$ ), with lauric acid ( $\blacksquare$ ), and after 12 hr of storage ( $\blacktriangle$ ).



**Fig. 5.** Effects of lauric acid and storage on  $\tan \delta$  of TNuS19 rice starch gels during heating: gel without lauric acid ( $\blacklozenge$ ), with lauric acid ( $\blacksquare$ ), and after 12 hr of storage ( $\blacktriangle$ ).



**Fig. 4.** Effects of lauryl alcohol and storage on dynamic viscosity ( $\eta'$ ) of TNuS19 rice starch gels during heating: gel without lauryl alcohol ( $\diamond$ ), with lauryl alcohol ( $\square$ ), and after 12 hr of storage ( $\Delta$ ).



**Fig. 6.** Effects of lauryl alcohol and storage on  $\tan \delta$  of TNuS19 rice starch gels during heating: gel without lauryl alcohol ( $\diamond$ ), with lauryl alcohol ( $\square$ ), and after 12 hr of storage ( $\Delta$ ).

ing time in all cases. Also, the percentages of reversibility were higher for polar complexes (Table III) as compared with nonpolar complexes (Table IV). This suggests that a more perfect partially crystalline structure due to annealing and complexation with polar ligands gave a higher percentage of reversible realignment.

#### Effects of Complexing Agent and Storage on Rheological Properties

It is well known that starch gels are nonequilibrium systems (Slade and Levine 1987, Biliaderis and Juliano 1993). Retrogradation of starch gel on storage reflects contributions from diffusion-controlled chain-folding processes (Biliaderis 1992). Dynamic rheological properties investigated by small-amplitude oscillatory shear measurements are particularly useful in monitoring the molecular organization in the gelation process (Durand et al 1990). They also provide further insight into segment movement of the gel network (they demonstrate rheological responses that reflect the viscoelastic characteristics of the gels) (Biliaderis 1992). Thus, phase transitions of the gels can also be monitored.

When measured by a dynamic rheometer, both  $G'$  and  $G''$  moduli of all gels showed little dependence on frequency within the range of 0.1–2.5 Hz at 30°C (data not shown). This indicates that no major relaxation processes occurred over this range of

frequencies. Therefore, all measurements were obtained at a fixed frequency of 1 Hz. The  $G'$  of the TNuS19 rice starch gel showed a linear dependence on concentration up to 6%. The  $G'$  of gels with added polar ligands were higher than that for the control (no ligand added) during heating (Figs. 1 and 2). The  $G'$  of the complexed gel increased further during 12 hr of storage. These data revealed that the elastic structure (junction zones) of the starch gel (mainly amylose) could be strengthened by complex formation and further reinforced during storage. Note that the  $G'$  of the stored, complexed gel with LA was higher than that with LOH (Figs. 1 and 2), indicating that the storage effect on the network structure was more pronounced for the complexed gel with LA than that with LOH.

The dynamic viscosity ( $\eta'$ ) of rice starch gel also increased with the addition of ligand and with 12 hr of storage (Figs. 3 and 4). This finding concurred with the report of Biliaderis and Tonogai (1991). It is likely that there was only limited amylose leaching in the concentrated gels compared with that in the diluted dispersions. To some extent, the leached amylose was complexed with added ligand, which was added to the gel network during mixing and annealing at 85°C. During the initial stage of the cooling process, only a limited amount of leached amylose could have had the chance to interact with other molecules in the concentrated gel system. Therefore, there was a tendency for inter-

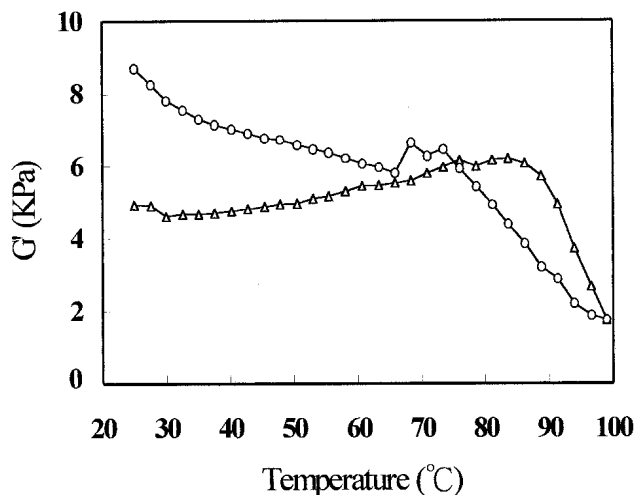


Fig. 7. Changes in storage moduli ( $G'$ ) of TNuS19 rice starch-lauryl alcohol gel with 12 hr of storage during heating ( $\Delta$ ) and cooling ( $\circ$ ).

molecular association (including amylopectin and amylose) to continue during storage, causing a further increase of dynamic viscosity. According to the results in Figs. 5 and 6,  $\tan \delta$  of the complexed gels without storage was less than that of the control at temperatures  $>40^\circ\text{C}$ , and both were  $<0.1$ , which is considered the behavior of a well-crosslinked gel (Biliaderis and Juliano 1993). However,  $\tan \delta$  of the complexed gel became  $>0.1$  after 12 hr of storage, which was taken as an indication of gel weakening. Results from breaking-stress studies of starch-lipid complexation in potato, wheat, and maize starch gels (Conde-Petit and Escher 1994) seemed contrary to the above findings. The gel instability observed here could be due to the incompatibility between molecules of amylose and amylopectin in the gel during storage (Kalichevsky and Ring 1987, German et al 1992). This phenomenon is commonly associated with aggregation of similar molecules and separation of dissimilar molecules, ending up in phase separation. Also, water near the two polymeric components was exuded to the outer surface of the starch gel network during aging, and thus, the limited amount of surrounding water might not have been enough to hydrate both incompatible components (Chien 1993). Eventually, incompatibility processes were likely to proceed during storage in addition to the strengthening of the gel network.

The  $G'$  increased slowly while the rice starch-LOH complex was heated from 25 to  $85^\circ\text{C}$  and then decreased dramatically during further heating from 85 to  $100^\circ\text{C}$  (Fig. 7). The decrease of  $G'$  may have been due to disruption of the gel structure during heating (Kim et al 1992) or to evaporation of water from the gel. During cooling,  $G'$  increased slowly and the gels reverted to an elastic structure. During cooling from 80 to  $70^\circ\text{C}$ ,  $G'$  showed a peak, suggesting the formation of a complex. The above results showed that complexation, to a large extent, was reversible.

With these overall composite characteristics and the polarity of the added ligands, annealing or a storage process was able to change the thermal and rheological properties of these rice starch gels.

#### ACKNOWLEDGMENTS

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