

# Composition Dependencies of the Rheological Properties of Rice Starch Blends

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ABSTRACT

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The gelatinization, pasting, and dynamic rheological parameters of rice starch dispersions from Kaoshiung Sen 7 (KSS7), Taichung Waxy 70 (TCW70), and their blends were examined in relation to total starch concentration ( $C_t$ ) and the property of starch components. Mixing the rice starches, especially at equivalent ratios, resulted in decreasing onset temperature for gelatinization or developing viscosity and in cold-paste viscosity, accompanied by a synergistically increased peak viscosity. The logarithmic of storage moduli,  $G'$ , for all starch dispersions except the retrograded systems of  $C_t = 20$ –30 wt%, showed two linear dependencies on the weight-average amylose content (AC) of the blends separating at a

critical AC of 20 wt% (i.e., TCW70 = 25 wt%). Interestingly, the temperatures at which  $G'$  started to increase drastically maximized on heating, and the exponent  $n$  of  $G' \propto C_t^n$  also maximized at the same TCW70 starch concentration. Generally, the elasticity of the systems after complete gelatinization and retrogradation followed the isostress models of Takayanagi's blending laws at  $C_t = 10$  wt%, but changed to the intermediates of isostress and isostrain at  $C_t = 20$ –30 wt%. The changes in these parameters can be explained by competitive swelling behavior, the strengthening effect of swollen granules, and shear disintegration.

Generally, starch granules in sufficient moisture undergo gelatinization on heating, associating with granular swelling, disintegration and crystalline melting, and retrogradation or setback on cooling or aging (Eliasson 1986; Keetels and van Vliet 1994; Lii et al 1995, 1996ab; Tsai et al 1997). The rheological feature of such starch dispersions can be explained by leached materials such as the continuous matrices with granular remnants as the dispersed "fillers" (Eliasson 1986) and, to some extent, relating to the amylose content, starch concentration (Biliaderis and Zawistowski 1990; Biliaderis and Juliano 1993; Lii et al 1996ab), and thermal or shearing treatment (Ortega-Ojeda and Eliasson 2001; Chen et al 2003). For concentrated starch dispersions, especially at <30% water content, the mechanical properties are further governed by events such as water-dependent glass transition in the amorphous regions within granule and annealing or recrystallization in the vicinity of crystalline regions (Biliaderis et al 1986; Kalichevsky and Blanshard 1993).

Native starch blends are increasingly applied in food industry to make starchy foods with a desired rheological property, texture, or storage stability, or to replace modified starch (Obanni and BeMiller 1997). In contrast to single starch systems, starch blends generally exhibit unique viscoelastic or physical properties that cannot be directly interpreted by the final apparent amylose content or mixing ratio (Obanni and BeMiller 1997; Lin et al 2002). This may be because of the differences in swelling and solubility properties between dissimilar starches (Liu and Lelièvre 1992a; Ortega-Ojeda and Eliasson 2001; Chen et al 2003) and the uncertainties involved in intermolecular association (del Rosario and Pontiveros 1983; Obanni and BeMiller 1997; Lin et al 2002). The interactions between starch materials that control the texture-related structure of starch composites in food are dependent on the experimental or processing conditions.

The modulus-composition relationship for the polymer composites without interactions between the different phases can be theoretically explored with the simplified isostrain and isostress blending laws of Takayanagi et al (1963). The isostrain model is suitable for describing the elasticity of a composite (C) containing a stronger continuous matrix (X) dispersed with weak particles (Y). The overall elasticity of the isostrain composite approximates

the weight-average elasticity of the individual elasticity:  $G'_C = G'_X\phi_X + G'_Y\phi_Y$ , where  $G'_X > G'_Y$ ,  $\phi_X$  and  $\phi_Y$  are the weight fractions (or volume fractions as the density of the systems = 1 g/mL) of the continuous and dispersed phases ( $\phi_X + \phi_Y = 1$ ). On the other hand, the isostress model works better with weak matrices and strong fillers and has an overall compliance equal to the weight-average compliance of the individual compliances ( $1/G'_C = \phi_X/G'_X + \phi_Y/G'_Y$ , where  $G'_X < G'_Y$ ). Previous investigations on blending rules in food biopolymer mixtures have been on potato starch-amylose mixed gels (Svegmark and Hermansson 1993), starch-gelatin composites (Abdulmola et al 1996a), and blends of cross-linked waxy starch and xanthan gum (Abdulmola et al 1996b). Nonetheless, the viscoelastic properties of starch mixes have not been investigated with respect to these blending rules, especially for starch mixes with distinct gelatinization behaviors (Liu and Lelièvre 1992a; Obanni and BeMiller 1997; Chen et al 2003) or with noticeable interactions between granules and soluble materials frequently present in starch mixes containing amylose (Svegmark and Hermansson 1993; Tsai and Lii 2000).

The aim of this work was to clarify the rheological changes of starch blend dispersions with varying blending ratio and phase properties of individual starch species. One high-amylose indica rice starch and one waxy rice starch were examined because of their obviously different swelling-solubility property and retrogradation tendency but similar original granular sizes (Lii et al 1995, 1996ab). The applicability of the Takayanagi's blending laws for the rice starch blends are discussed in relation to the gelatinization and retrogradation behaviors of the starches involved.

## MATERIALS AND METHODS

### Sample Preparation

Rice starches from Kaoshiung Sen 7 (KSS7, indica type) and Taichung Waxy 70 (TCW70, waxy type) were isolated by the modified alkaline steeping method (Yang et al 1984). The KSS7 and TCW70 starches have an apparent amylose content (AC) of 25.6 and 1.0%, respectively (Lii et al 1995). The KSS7 and TCW70 blends were prepared at ratios of 85:15, 75:25, 50:50, 25:75, and 15:85 (w/w).

### Measurement of Thermal Properties During Gelatinization

Differential scanning calorimetry (DSC) analysis was performed using a DSC 2910 differential scanning calorimeter (TA Instruments, Surrey, England) equipped with a refrigerated cooling system. A portion (8–10 mg) of well-mixed starch suspensions at total starch concentrations ( $C_t$ ) of 20, 30, and 40 wt% were weighed into a hermetically sealed aluminum pan and detected from 20 to 140°C at 5°C/min (Lai and Lii 1999). The onset ( $T_o$ ), peak ( $T_p$ ), and

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conclusion ( $T_c$ ) temperatures, gelatinization temperature ranges ( $GT = T_c - T_o$ ), as well as enthalpy changes ( $\Delta H$ , on dry starch basis) during gelatinization of starch blends were measured in three replicates.

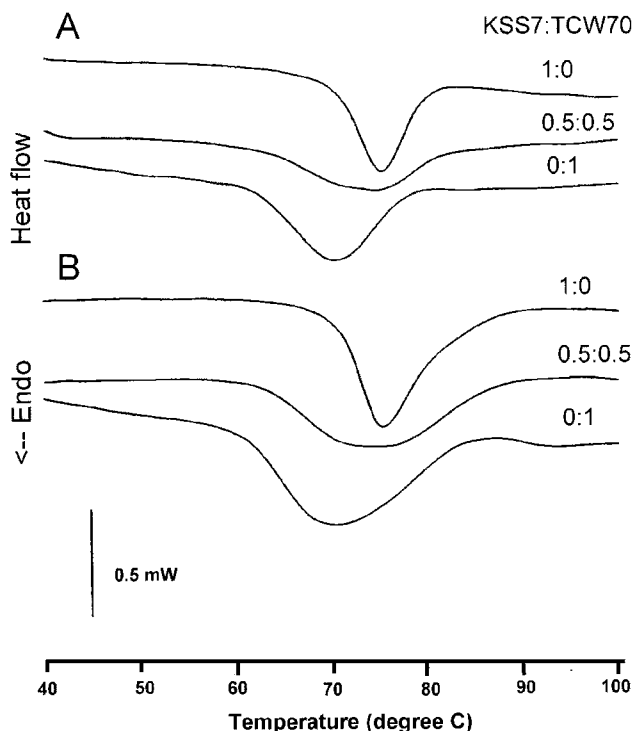
### Measurement of Pasting Properties

The pasting property of starch suspensions (8 wt%, 25 mL) was measured in a Rapid Visco Analyser (RVA 4D, Newport Scientific Pty., Ltd, Narrabeen, Australia) with an aluminum RVA canister and a paddle rotated at 160 rpm. The temperature program exerted

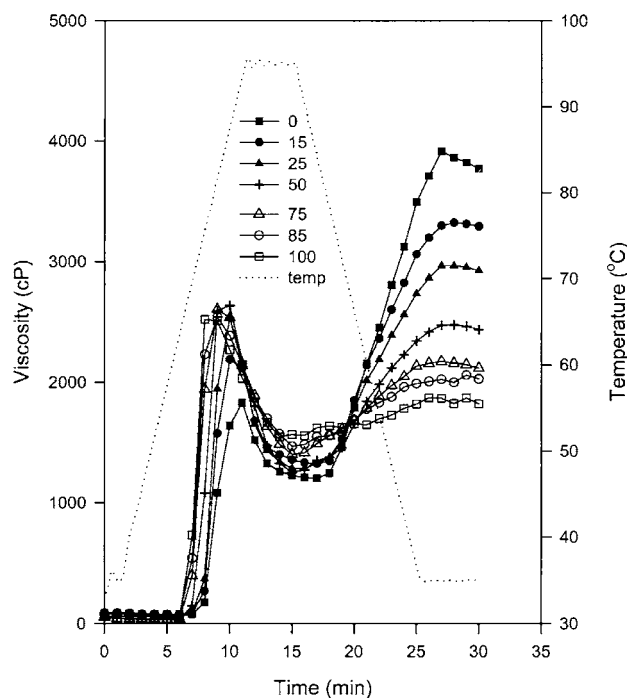
on the sample was holding at 35°C for 1.5 min, heating to 95°C at 6°C/min, holding at 95°C for 4 min, cooling to 35°C at 6°C/min, and holding at 35°C for 5 min (Lai et al 2001).

### Measurement of Rheological Properties

Small amplitude oscillatory rheological measurements were performed on a rheometer (Carri-Med CSL 100, TA Instruments) equipped with parallel-plate geometry (20 mm in diameter). The gap size was 1,000  $\mu\text{m}$ , strain was 0.5%, and frequency was 1 Hz. A portion of thoroughly dispersed starch suspensions was immediately loaded onto the peltier of the rheometer, then covered with a layer of light silicone oil at the exposed edge of sample to prevent



**Fig. 1.** Heat flow changes during gelatinization of KSS7, TCW70, and a blend at total starch concentration ( $C_t$ ) = 20 wt% (A) and 40 wt% (B). Ratios in w/w.



**Fig. 2.** Rapid viscosity profiles of 8 wt% starch suspensions by RVA analysis (heating and cooling rates 6°C/min, stirring speed 160 rpm; wt% of TCW70 replacing KSS7 starch).

**TABLE I**  
Differential Scanning Calorimetric (DSC) Characteristics<sup>a</sup> for Gelatinization of KSS7, TCW70 Rice Starches and Their Blends

Concentration ( $C_t$ , wt%)	TCW70 (%)	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)	GT (°C)	$\Delta H$ (J/g)
20	0	70.3 ± 0.0a <sup>b</sup>	75.2 ± 0.2a	82.7 ± 0.3cd	12.3 ± 0.3e	15.0 ± 0.4b
	15	68.9 ± 0.1b	75.0 ± 0.1a	85.7 ± 1.2ab	16.8 ± 1.1d	14.6 ± 0.8b
	25	67.1 ± 0.6c	75.0 ± 0.2a	87.9 ± 1.8a	20.8 ± 2.3bc	15.0 ± 0.4b
	50	62.8 ± 0.4d	74.2 ± 0.3b	86.2 ± 0.7ab	23.4 ± 0.8a	17.0 ± 0.3a
	75	62.3 ± 0.5d	71.3 ± 0.6c	84.1 ± 1.5bc	21.8 ± 1.2ab	17.4 ± 0.4a
	85	62.3 ± 0.4d	70.9 ± 0.2cd	81.3 ± 1.3de	18.9 ± 1.1cd	15.0 ± 0.1b
30	100	62.2 ± 0.2d	70.5 ± 0.2d	79.7 ± 0.5e	17.5 ± 0.4d	15.1 ± 0.6b
	0	70.1 ± 0.1a	75.1 ± 0.3a	84.9 ± 0.8ab	14.8 ± 0.7e	14.5 ± 0.5a
	15	69.0 ± 0.2b	75.3 ± 0.1a	85.7 ± 0.8ab	16.7 ± 0.8d	14.3 ± 0.6a
	25	67.6 ± 0.2c	75.2 ± 0.2a	85.1 ± 1.4ab	17.5 ± 1.5d	13.8 ± 1.3a
	50	63.0 ± 0.3d	74.2 ± 0.2b	86.0 ± 0.7a	23.0 ± 0.6ab	14.6 ± 0.2a
	75	61.9 ± 0.3e	70.8 ± 0.2c	84.2 ± 1.2b	22.2 ± 1.5b	13.7 ± 0.6a
40	85	61.6 ± 0.1ef	70.6 ± 0.3c	85.9 ± 0.4a	24.3 ± 0.3a	14.6 ± 1.0a
	100	61.2 ± 0.2f	70.0 ± 0.3d	81.0 ± 0.1c	19.7 ± 0.1c	13.9 ± 0.6a
	0	70.8 ± 0.0a	75.1 ± 0.1a	90.2 ± 0.8a	20.2 ± 0.7d	13.5 ± 0.2b
	15	67.8 ± 0.3b	75.0 ± 0.1a	89.0 ± 0.7bc	21.2 ± 0.5d	14.4 ± 0.5ab
	25	65.0 ± 0.2c	75.1 ± 0.2a	89.5 ± 0.7ab	24.5 ± 0.5b	14.7 ± 0.8a
	50	63.5 ± 1.4d	74.3 ± 0.9b	89.2 ± 0.8ab	26.0 ± 1.1a	14.5 ± 0.9ab
	75	61.7 ± 0.1e	70.8 ± 0.2c	87.9 ± 0.5cd	26.1 ± 0.4a	14.7 ± 0.2a
	85	61.2 ± 0.1e	70.3 ± 0.1cd	87.5 ± 0.8d	26.3 ± 0.8a	14.3 ± 0.2ab
	100	60.7 ± 0.1e	69.9 ± 0.3d	83.9 ± 0.4e	23.1 ± 0.5c	14.3 ± 0.2ab

<sup>a</sup>  $T_o$ ,  $T_p$ ,  $T_c$ , GT, and  $\Delta H$  = onset, peak, and conclusion temperatures, and gelatinization temperature range ( $GT = T_c - T_o$ ) and enthalpy change, respectively.

<sup>b</sup> Mean values ± standard deviations ( $n = 3$ ). Means with different letters within the same column at the same total starch concentration ( $C_t$ ) are significantly different ( $P < 0.05$ ).

water evaporation. The samples were then scanned consecutively during heating (from 45 to 95°C at 1°C/min), cooling (from 95 to 25°C at 2.5°C/min) and aging (at 25°C for 1 hr) (Tsai and Lii 2000). The rheological parameters including storage ( $G'$ ) and loss ( $G''$ ) moduli and loss tangent ( $\tan \delta$ ) were collected in three replicate measurements.

### Statistical Analysis

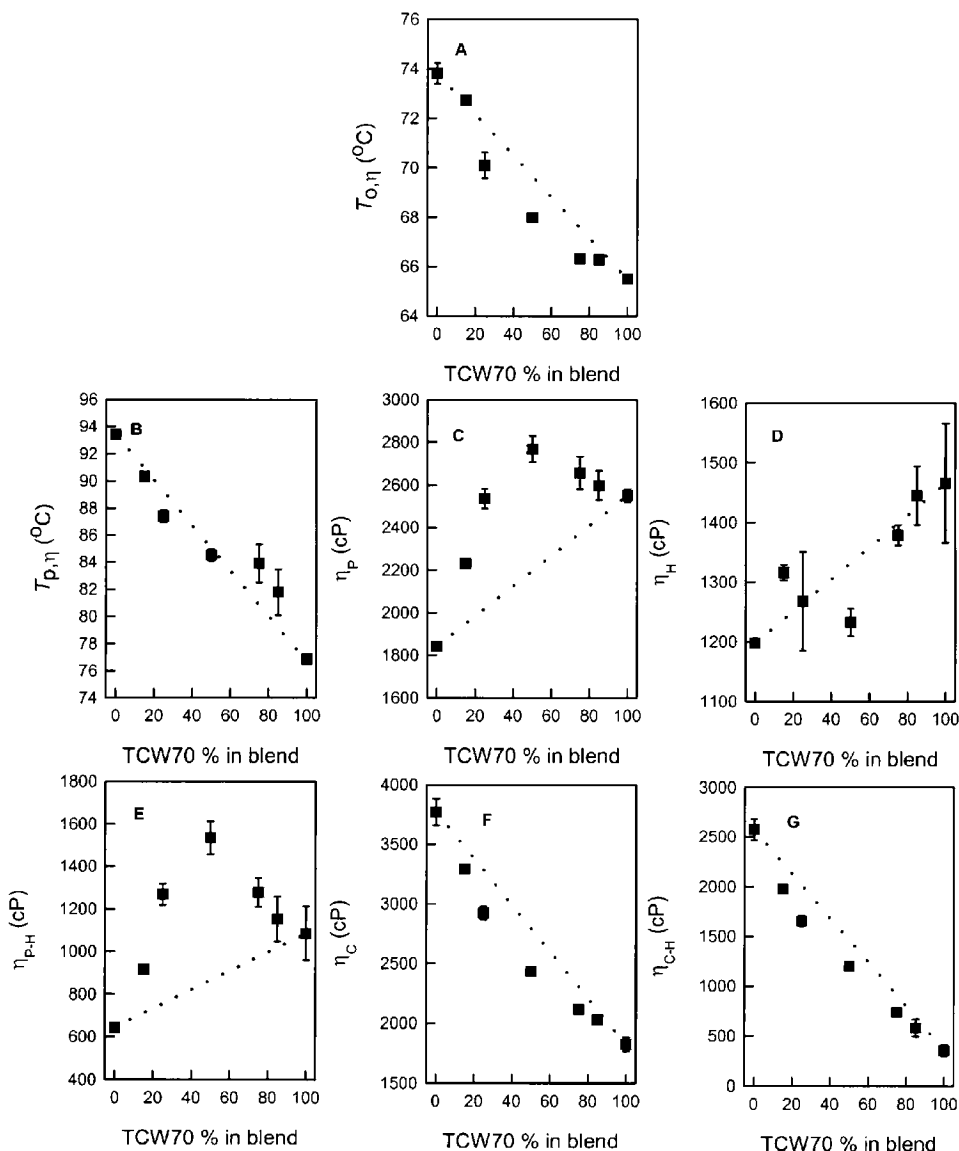
Analysis of variance (ANOVA) and the significance of differences among samples (Duncan's multiple range test) were analyzed using SAS for Windows R 6.12 (SAS Institute Inc., Cary, NC).

## RESULTS AND DISCUSSION

### Gelatinization Properties of Starch Blends

Figure 1 displays the heat flow changes during gelatinization of some starch systems exemplified at  $C_1 = 20$  (A) and 40 wt% (B). Generally, all systems studied showed single endothermic peaks during gelatinization that were broader at a higher  $C_1$  for TCW70 rather than KSS7, and for blends rather than pure starches. The thermal parameters for onset ( $T_o$ ), peak ( $T_p$ ), and conclusion ( $T_c$ ) temperatures, gelatinization temperature range ( $GT = T_c - T_o$ ), as

well as enthalpy changes ( $\Delta H$ ) of the KSS7/TCW70 mixed suspensions at  $C_1 = 20, 30,$  and 40 wt% are shown in Table I. Typically, the pure KSS7 starch showed remarkably high  $T_o$  and  $T_p$  values, narrow  $GT$ , but  $\Delta H$  values comparable to those of the pure TCW70. When the TCW70 composition in the blend (TCW70%) was elevated to  $\approx 50$  wt%, the  $T_o$  leveled off, and  $T_p$  started to reduce significantly for all  $C_1$  ranges studied. The observed  $T_c$  tended to reach a peak at  $\approx 50\%$  TCW70 at low  $C_1$  (20 and 30 wt%); but  $T_c$  successively decreased with increasing TCW70% at high  $C_1$  (40 wt%). The  $GT$  maximized at 50 wt% TCW70, probably due to the additive results of gelatinization of two starch components. The  $\Delta H$  varied insignificantly between most of starch blends. But those containing 50 or 75 wt% TCW70 only at  $C_1 = 20$  wt% displayed a significantly greater  $\Delta H$ , perhaps relating to the artificial error of integration because microcrystallites within starch granules may melt independently at that moisture content. Similar results in  $\Delta H$  are also found for most of the mixtures from any two of potato, barley, and waxy maize starches (Ortega-Ojeda and Eliasson 2001). Effects of exothermic lipid-amylose complexation within granules on the endothermic gelatinization parameters (Biliaderis et al 1986; Biliaderis and Juliano 1993) are difficult to clarify in these blends.

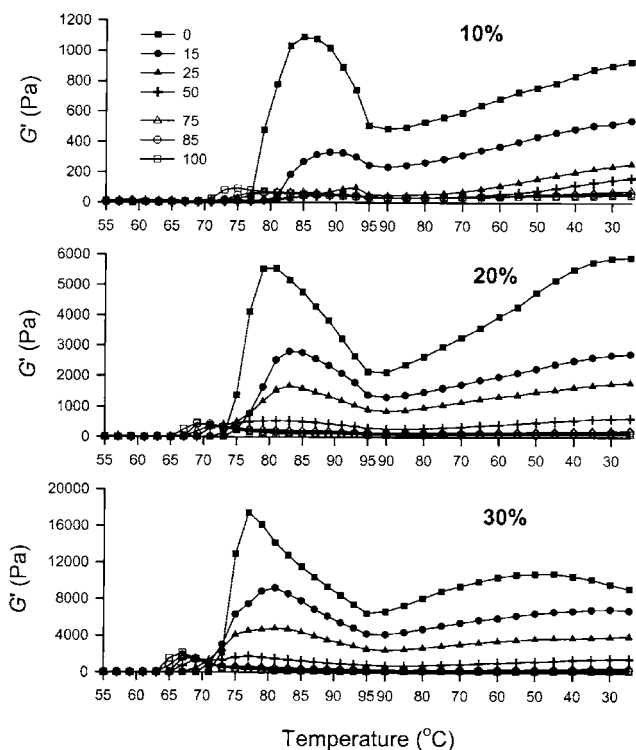


**Fig. 3.** Effects of TCW70 composition on pasting parameters of KSS7/TCW70 blend suspensions examined by RVA. A,  $T_{o,\eta}$  onset and B,  $T_{p,\eta}$  peaks for rapid viscosity. C,  $\eta_p$  peak, and D,  $\eta_H$  hot-paste, and E,  $\eta_C$  cold-paste viscosities. E,  $\eta_{p-H}$  breakdown; G,  $\eta_{C-H}$  total setback. Total starch concentration 8 wt%.

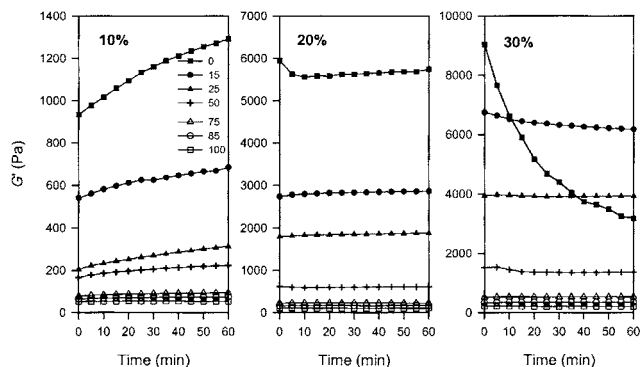
## Pasting Properties of Starch Blends

The rapid viscosity profiles of 8 wt% starch blend suspensions during RVA measurements are shown in Fig. 2. In comparison with the pure KSS7, the TCW70 exhibited a higher peak viscosity ( $\eta_p$ ) followed by a more notable viscosity breakdown due to the shearing-induced disintegration of swollen granules (i.e., shear thinning) (Subrahmanyam and Hoseney 1995; Chen et al 2003) and a lower setback on cooling. It is notable that the  $\eta_p$  was mainly governed by TCW70 even as low as 15 wt%; while the hot-paste ( $\eta_H$ ) and cold-paste ( $\eta_C$ ) viscosities changed successively with increasing TCW70%.

The pasting parameters of the TCW70% starch blend suspensions, including the onset and peak temperatures ( $T_{o,\eta}$  and  $T_{p,\eta}$ , respectively), peak viscosity ( $\eta_p$ ), hot-paste viscosity ( $\eta_H$ ), breakdown ( $\eta_{p-H}$ ), cold-paste viscosity ( $\eta_C$ ), and setback ( $\eta_{C-H}$ ), are illustrated in Fig. 3. Increasing TCW70% made the RVA parameters

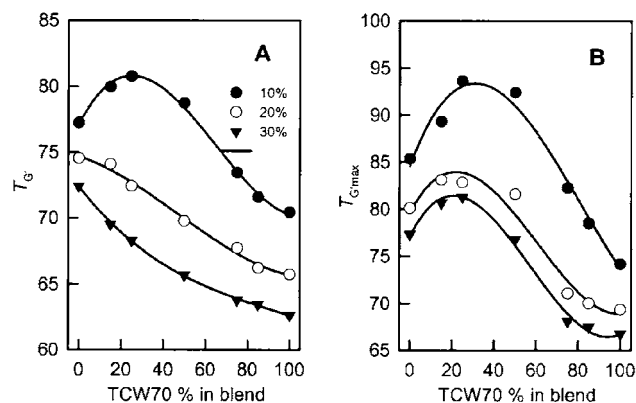


**Fig. 4.** Developments in storage modulus ( $G'$ ) during heating and subsequent cooling processes of starch suspensions prepared from KSS7, TCW70, and their blends at total starch concentrations of 10–30 wt% (heating rate 1.0 $^{\circ}\text{C}/\text{min}$ , cooling rate 2.5 $^{\circ}\text{C}/\text{min}$ , frequency 1 Hz, strain 0.5%, wt% of TCW70 replacing KSS7 starch).

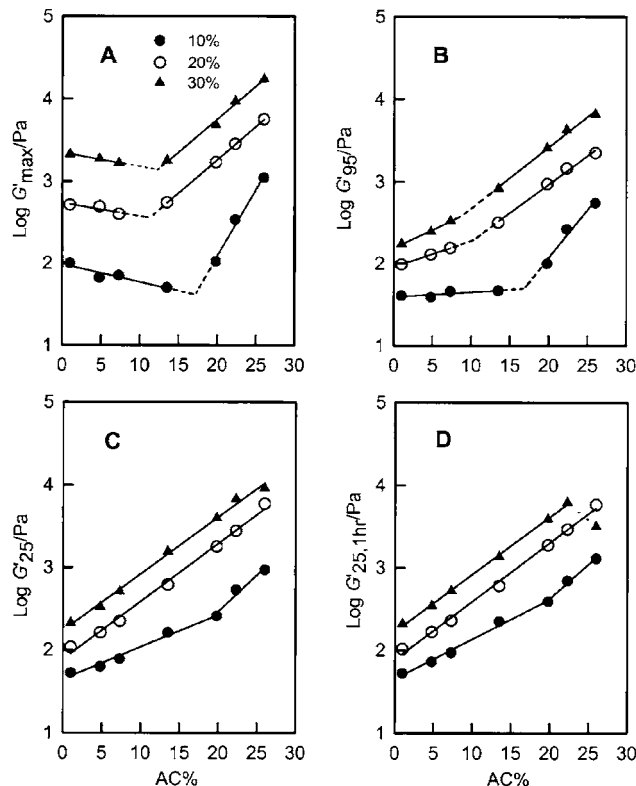


**Fig. 5.** Storage modulus ( $G'$ ) profiles of gelatinized starch suspensions prepared from KSS7, TCW70, and their blends during aging at 25 $^{\circ}\text{C}$  for 1 hr. Measuring conditions as in Fig. 4.

essentially shift from those of KSS7 to those of TCW70. In comparison with the theoretical weight-average properties of individual starches (dotted lines in Fig. 3), there is an approximately linear relationship between  $T_{p,\eta}$  or  $\eta_H$  and TCW70 content. The  $T_{o,\eta}$ ,  $\eta_C$ , and  $\eta_{C-H}$  responded slightly concavely with increasing TCW70 content; while  $\eta_p$  and  $\eta_{p-H}$  significantly overshoot those of weight-averages of the two starches. The tendencies of  $T_{o,\eta}$  and  $T_{p,\eta}$  for TCW70 content were different from those of  $T_o$  and  $T_p$  from DSC (Table I). Mixing the rice starches, especially at a 50:50 ratio, resulted in reduced  $T_{o,\eta}$ ,  $\eta_C$ , and  $\eta_{C-H}$  and noticeably increased  $\eta_p$  and  $\eta_{p-H}$ . The compositional dependencies of  $\eta_p$  in regular RVA programs are similar to those previously examined in isothermal RVA programs at 85–95 $^{\circ}\text{C}$  (Chen et al 2003). However, the compositional dependencies of  $\eta_H$  were contrary to final hot paste



**Fig. 6.** Changes in temperatures at which storage modulus ( $G'$ ) started to increase and maximized. A,  $T_G$  and B,  $T_{G,max}$  with TCW70 composition of starch suspensions prepared from KSS7, TCW70, and their blends. Total starch concentrations in wt%. Measuring conditions as in Fig. 4.



**Fig. 7.** Changes in storage modulus ( $G'$ ) with reconstituted amylose contents (AC%) of starch suspensions prepared from KSS7, TCW70, and their blends. A,  $G'_{max}$  B,  $G'_{95}$  C,  $G'_{25}$  and D,  $G'_{25,1hr}$ .  $G'$  maxima and  $G'$  values at 95, 25, and holding at 25 $^{\circ}\text{C}$  for 1 hr, respectively. Total starch concentrations in wt%. Measuring conditions as in Fig. 4.

viscosities of the same starch blend suspensions after extensive disintegration by isothermal stirring for 30 min (Chen et al 2003).

### Dynamic Rheological Properties of Starch Blends

Figure 4 shows the compositional effects on the storage moduli ( $G'$ ) of mixed KSS7/TCW70 dispersions during heating and cooling processes at  $C_t = 10, 20,$  and  $30$  wt%. As expected, the  $G'$  of the starch dispersions increased with the  $C_t$  during the heating and cooling process. The high  $G'$  value for the high-amylose starch (KSS7) was remarkably reduced by replacement with the waxy starch (TCW70), the most remarkable reducing effect occurred at a lower  $C_t$ . For example, the incorporation of 15 wt% TCW70 caused the  $G'$  maximum on heating ( $G'_{max}$ ) to reduce to  $\approx 33\%$  and 50% of the pure KSS7 systems at  $C_t = 10$  wt% and 20–30 wt%, respectively. When starch dispersion systems were cooled, the systems with higher TCW70% generally had a lower increasing rate in  $G'$  and greater  $\tan \delta$  value (lower retrogradation tendency). Increasing  $C_t$  generally led to a notable retrogradation and syneresis tendency, suggested by the  $G'$  reduction on cooling to  $<40^\circ\text{C}$  (Lii et al 1995).

Figure 5 shows the composition-dependent rheological changes of the gelatinized starch blends on short-term aging. At  $C_t = 10$  wt%, the  $G'$  increases due to the retrogradation of gelatinized KSS7 were observed even when 50 wt% of KSS7 was replaced with TCW70. At  $C_t = 20$  wt%, the  $G'$  decrement related to syneresis for the pure KSS7 starches was not observed in the other systems containing TCW70. No significant retrogradation or syneresis (suggested by constant  $G'$  values during short-term aging) were found for the systems of  $C_t \geq 20$  wt% and when TCW70 content was  $\geq 25$  wt%. Accordingly, in this study, the lowest TCW70 content required to stabilize the KSS7-dominant systems at  $C_t = 30$  wt% was  $\approx 25$  wt%. Similar advantages in preventing syneresis had also been reported by using blends of unmodified pea and corn starches (Stute and Kern 1994). The interactions of amylose and amylopectin may be responsible for the reduced retrogradation or syneresis of the mixtures.

The critical temperatures at which starch granules started to pack closely ( $T_G$ ) and reached a maximal  $G'$  ( $T_{G_{max}}$ ) during heating (Lii et al 1996b; Tsai et al 1997) are illustrated in Fig. 6A and B, respectively, as a function of TCW70 content in the blend. Higher  $C_t$  accompanied lower values in  $T_G$  and  $T_{G_{max}}$ . At low  $C_t$

(10 wt%), the  $T_G$  reached a maximum at TCW70% = 25 wt%, reflecting the contribution of high-swelling TCW70 starch. But this was not true for those at higher concentrations ( $C_t = 20$ –30 wt%) and under restricted swelling conditions, of which the  $T_G$  decreased constantly with increasing TCW70 content. Interestingly, the  $T_{G_{max}}$  maximized at 25 wt% TCW70 as well as for all  $C_t$  examined. The compositional dependencies of  $T_G$  and  $T_{G_{max}}$  at  $C_t = 10$  wt% obtained with negligible interference were evidently different from those of the  $T_{o,\eta}$  and  $T_{p,\eta}$  detected under extensive shearing and at  $C_t = 8$  wt% (Fig. 3A and B). The critical TCW70% of maximal  $T_G$  and  $T_{G_{max}}$  agrees completely with that of swelling decrement found previously (Chen et al 2003).

The loss tangent results (Table II) indicated that at  $G'_{max}$ , the greatest viscous property (i.e., greatest  $\tan \delta_{max}$ ) for the blends were found when 50 wt% KSS7 was replaced with TCW70, regardless of the  $C_t$  examined. This observation also held true for the gelatinized low  $C_t$  (10 wt%) slurry heated to  $95^\circ\text{C}$ . However, for all other blends after gelatinization and retrogradation,  $\tan \delta$  values (including  $\tan \delta_{95}$ ,  $\tan \delta_{25}$  and  $\tan \delta_{25,1hr}$ ) increased significantly and successively with decreasing TCW70 content. For starch blends with  $\geq 75$  wt% TCW70, higher  $C_t$  caused greater rather than lower  $\tan \delta_{25}$  (and  $\tan \delta_{25,1hr}$ ).

### Effects of Apparent Amylose Content (AC)

Apparent amylose content (AC) has been used as an index for assessing the texture or eating quality of starch and rice products (Radhika Reddy et al 1994; Juliano 1998; Lii et al 1998). How storage moduli ( $G'_{max}$ ,  $G'_{95}$ ,  $G'_{25}$ , and  $G'_{25,1hr}$ ) of the starch blend suspensions respond with respect to the weight-average AC of the blends (Fig. 7) will be of great interest. A logarithmic plot of  $G'_{max}$  against AC (Fig. 7A) showed two linear sections intersecting at critical AC between 12 and 17 wt% (TCW70% = 35–65 wt%), with increasing  $C_t$  from 10 to 30 wt%. Similar observations were made for the  $G'_{95}$  plot (Fig. 7B) but with lower slopes at all  $C_t$  levels. For retrograded systems, AC dependencies of logarithmic  $G'_{25}$  (Fig. 7C) and  $G'_{25,1hr}$  (Fig. 7D) remained with two linearities at  $C_t = 10$  wt% intersecting at AC = 20 wt% (25 wt% TCW70). However, only one single linear relationship existed at higher  $C_t$  (20–30 wt%), except the  $G'_{25,1hr}$  at AC = 25.6% (pure KSS7) and  $C_t = 30$  wt% due to the remarkable syneresis mentioned (Fig. 5).

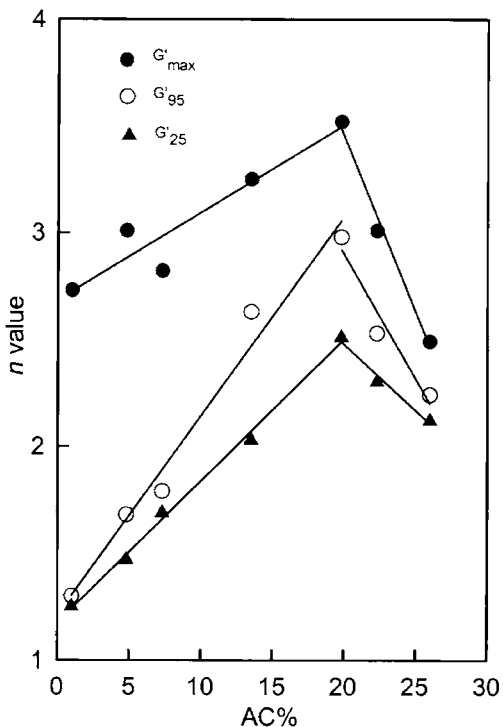
TABLE II  
Loss Tangents<sup>a</sup> of KSS7, TCW70 Rice Starches, and Their Blends During Heating-Cooling-Aging Processes<sup>b</sup>

Concentration ( $C_t$ , wt%)	TCW70%	Tan $\delta_{max}$	Tan $\delta_{95}$	Tan $\delta_{25}$	Tan $\delta_{25,1hr}$
10	0	0.08 ± 0.00d <sup>c</sup>	0.12 ± 0.01d	0.05 ± 0.01d	0.03 ± 0.00e
	15	0.13 ± 0.00c	0.14 ± 0.01cd	0.08 ± 0.01d	0.07 ± 0.00d
	25	0.20 ± 0.03bc	0.20 ± 0.04cd	0.16 ± 0.04c	0.12 ± 0.02c
	50	0.40 ± 0.16a	0.39 ± 0.15a	0.19 ± 0.03bc	0.15 ± 0.01b
	75	0.25 ± 0.09bc	0.26 ± 0.04b	0.22 ± 0.01ab	0.20 ± 0.01a
	85	0.28 ± 0.06a	0.27 ± 0.03b	0.23 ± 0.01a	0.20 ± 0.01a
20	100	0.21 ± 0.03bc	0.24 ± 0.01bc	0.24 ± 0.01a	0.22 ± 0.01a
	0	0.08 ± 0.00f	0.09 ± 0.00e	0.02 ± 0.00g	0.02 ± 0.00g
	15	0.12 ± 0.01e	0.11 ± 0.00d	0.06 ± 0.01f	0.06 ± 0.01f
	25	0.15 ± 0.00d	0.15 ± 0.00c	0.09 ± 0.00e	0.09 ± 0.00e
	50	0.21 ± 0.01a	0.20 ± 0.02b	0.15 ± 0.02d	0.17 ± 0.01d
	75	0.20 ± 0.01b	0.26 ± 0.00a	0.24 ± 0.02c	0.24 ± 0.02c
30	85	0.19 ± 0.01b	0.27 ± 0.01a	0.29 ± 0.02b	0.29 ± 0.02b
	100	0.16 ± 0.00c	0.27 ± 0.01a	0.34 ± 0.01a	0.34 ± 0.01a
	0	0.09 ± 0.00f	0.08 ± 0.00f	0.04 ± 0.00g	0.04 ± 0.00g
	15	0.11 ± 0.00e	0.10 ± 0.01f	0.08 ± 0.00f	0.08 ± 0.00f
	25	0.14 ± 0.00d	0.13 ± 0.01e	0.13 ± 0.01e	0.13 ± 0.01e
	50	0.20 ± 0.01a	0.22 ± 0.01d	0.21 ± 0.03d	0.26 ± 0.01d
	75	0.20 ± 0.00a	0.27 ± 0.02c	0.35 ± 0.01c	0.35 ± 0.02c
	85	0.19 ± 0.00b	0.29 ± 0.02b	0.41 ± 0.03b	0.41 ± 0.02b
	100	0.17 ± 0.01c	0.33 ± 0.02a	0.48 ± 0.02a	0.49 ± 0.02a

<sup>a</sup> Tan  $\delta_{max}$ , tan  $\delta_{95}$ , tan  $\delta_{25}$ , and tan  $\delta_{25,1hr}$  = loss tangents of the starch dispersions at  $G'_{max}$  and at  $95^\circ\text{C}$ ,  $25^\circ\text{C}$ , and after aging at  $25^\circ\text{C}$  for 1 hr, respectively.

<sup>b</sup> Heating and cooling rates were 1.0 and  $2.5^\circ\text{C}/\text{min}$ , respectively.

<sup>c</sup> Mean values ± standard deviations,  $n = 3$ . Means with different letters within the same column at the same total starch concentration are significantly different ( $P < 0.05$ ).



**Fig. 8.** Effects of reconstituted AC on exponent  $n$  ( $G' \propto C_1^n$ ) of starch suspensions prepared from KSS7, TCW70, and their blends. Moduli are defined in Fig. 7.

The exponents ( $n$ ) for  $G' \propto C_1^n$ , which theoretically concerns the number of cross-linking sites per junction zone (Clark 1992) for  $G'_{\max}$ ,  $G'_{95}$ , and  $G'_{25}$  at various blending ratios are shown in Fig. 8. Again, on average, two linear dependencies of the storage moduli on AC were observed; the lines intersected at their maximum at AC = 20 wt% (25 wt% TCW70). This tendency is quite different from the single linearity between  $n$  for  $G'_{25}$  and AC for a series of pure rice starch dispersions under similar heating and cooling conditions (Lai et al 2001). The  $n$  maximum at 25 wt% TCW70 in Fig. 8 could be partially attributed to a certain granular property. Because the exponents for  $G'$  after cooling are conclusively 3–7 for amylose gels (Ring 1985; Clark et al 1989; Biliaderis and Zawistowski 1990) and  $\approx 1$ –3 for starch systems (Biliaderis and Tonogai 1991; Biliaderis and Juliano 1993; Lii et al 1995; Lai et al 2001), the size of amylose chains besides AC and granular property would be also crucial to select a nonwaxy starch in starch blends. The  $n$  value may be one of indices for evaluating the texture of cooked rice and relative products that relates to AC as well (Juliano 1998).

#### Elastic Modulus-Composition Relationships

Figure 9 shows the effects of starch concentration and TCW70% on the observed  $G'_{\max}$ ,  $G'_{95}$ , and  $G'_{25}$  data of the above starch blends, in comparison with the isostrain (dotted lines, upper limits) and isostress (solid lines, lower limits) blending rules based on the concepts of Takayanagi et al (1963). The  $G'_{\max}$  (upper figures) of the blends with TCW70  $\geq$  25 wt% appeared below the isostress limits, especially at  $C_1 = 10$  wt%. This is perhaps the consequence of restricted swelling of the waxy starch when mixing with non-waxy starches (Chen et al 2003). For  $G'_{95}$  (middle figures), the data followed the isostrain rules at  $C_1 = 10$  wt% and shifted to the intermediate of isostrain and isostress limits at high  $C_1$  (20–30 wt%). Similar results were also observed for the  $G'_{25}$  parameters (lower figures). Accordingly, for the completely gelatinized systems, whether after retrogradation on cooling or not, the elastic moduli were theoretically a result of weak matrices and strong fillers at  $C_1 = 10$  wt% and of stronger matrices in contrast to the fillers at  $C_1 = 20$ –30 wt%.

#### Factors Influencing Rheological Properties

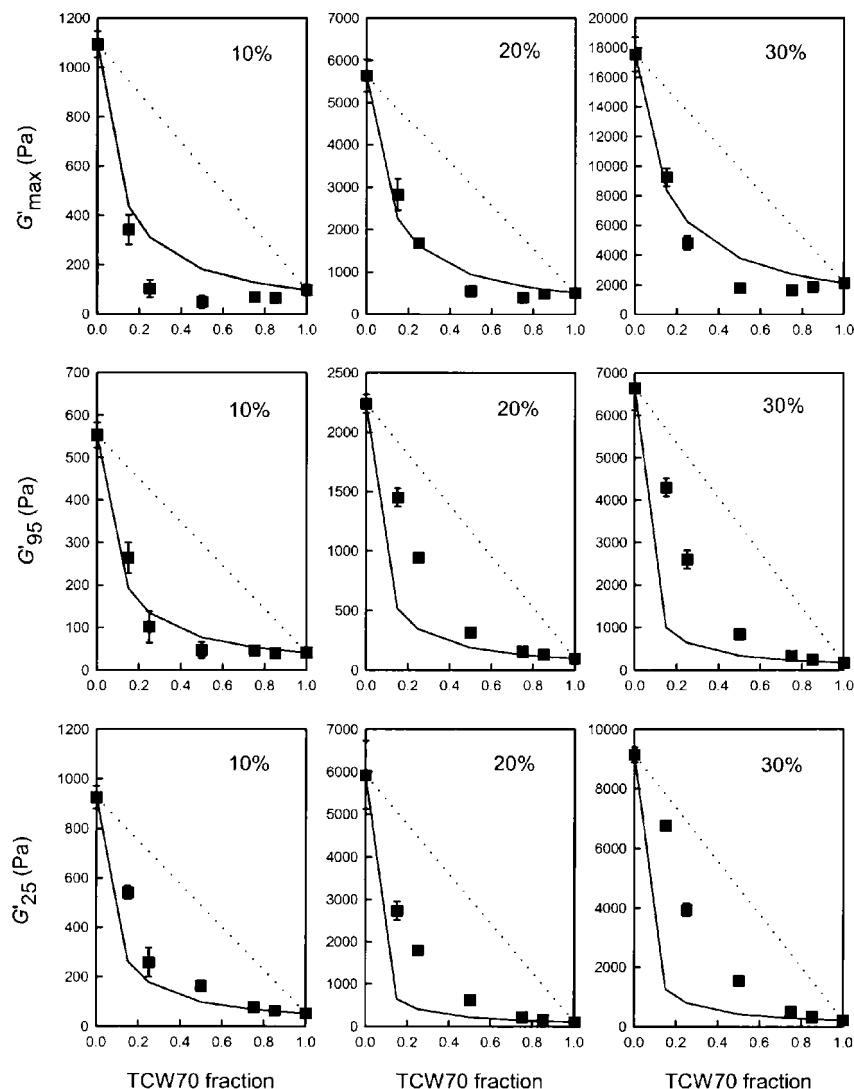
In view of RVA results (Fig. 3), the reduced  $T_{o,\eta}$ , increased  $\eta_p$  (and therefore  $\eta_{p-H}$ ), and reduced  $\eta_C$  (and therefore  $\eta_{C-H}$ ) when mixing the rice starches, especially at a 50:50 ratio, can be attributed to the competition for hydration between the unlike starches (Liu and Lelièvre 1992a; Chen et al 2003), the strengthening effects of swollen KSS7 granules in TCW70 matrices as fillers (Chen et al 2003), and the shear disintegration for the starch mixtures being more notable than that in single starch systems under extensive shear force (Chen et al 2003), respectively. Based on the reported solubilities (Lii et al 1995) and swelling powers of the two starches (Chen et al 2003), the swelling power and solubility of the 50:50 blend at  $T_{p,\eta}$  ( $\approx 85^\circ\text{C}$ ) can be estimated as 26 g/g and 12 wt%, respectively. This combination gave the estimated volume fraction of swollen granules ( $\phi_v$ ) at  $\approx 1.8$ , above which dispersed granules will start to disintegrate under shearing. The filler effects on increasing blend  $\eta_p$  during pasting at  $C_1 = 8$  wt% were also reported for the pastes prepared from mixtures of starches and polysaccharide gums (Liu and Lelièvre 1992b; Kulicke et al 1996), and for mixtures of amylose and amylopectin fractions from various botanical sources (Jane and Chen 1992).

At  $C_1 = 10$  wt%, the rice starch systems have equivalent values for  $T_{G'}$  and  $T_{\phi=1}$  (the temperature at which the swollen granules just closely contacted) (Lii et al 1996a). For such systems, the critical TCW70 content of 25 wt% at which  $T_{G'}$  and  $T_{G'_{\max}}$  maximized (Fig. 6) is identical to the composition at which a noticeable decrease in swelling occurred (Chen et al 2003). Accordingly, granular rigidity at this composition will be greater than those of other combinations. This could partially explain why blends with 25 wt% TCW70 had the greatest  $n$  value of  $G'_{25} \propto C_1^n$  (Fig. 8) and distinct retrogradation behaviors at  $\approx 25$  wt% TCW70 (20 wt% AC) (Fig. 7C). On the other hand, the ratio of KSS7 to TCW70 at  $\approx 2$ :1 (w/w) ( $\approx 17$  wt% AC) that  $G'_{\max}$  minimized (Fig. 7A) agrees with the reported composition at which the greatest degree of shear thinning occurred during pasting (Chen et al 2003).

For the concentrated systems of  $C_1 = 20$ –30 wt% (Figs. 7 and 8), the filler effects (Brownsey et al 1986; Liu and Lelièvre 1992b) were perceivable only from the exponent  $n$  of  $G' \propto C_1^n$  rather than from other parameters, different from  $C_1 = 10$  wt%. Stronger matrices, in contrast to the fillers, could be responsible for these differences. Other impacts from starch molecular properties (Jane and Chen 1992; Shibamura et al 1996; Lai et al 2001), lipid-amylose interactions (Biliaderis et al 1986; Biliaderis and Juliano 1993), thermal history during processing (Lii et al 1995) or shearing on pasting (Batey and Curtin 2000) may be considered when elucidating the rheology-composition relationship of starch mixtures. For more concentrated starch blends (at moisture contents of  $< 50$  or 30 wt% especially), effects of water plasticization (Biliaderis et al 1986) may be competitive between different amorphous regions of starch granules and needs to be emphasized.

#### CONCLUSIONS

When KSS7 and TCW70 rice starches were mixed and heated, each gelatinized individually but showed perceivably reduced onset temperatures for gelatinization and increased temperatures for initial development and maximization in storage moduli. Noticeable enhancing effects were observed for the peak viscosity ( $\eta_p$ ) especially when KSS7/TCW70 = 1:1 (w/w) and for the exponent  $n$  of  $G' \propto C_1^n$  when KSS7/TCW70 = 3:1 (w/w) (25 wt% TCW70 or weight-average AC = 20 wt%). At the latter composition, maximal  $T_{G'}$  and  $T_{G'_{\max}}$  and deviation in the composition dependence of  $G'$  were noted at  $C_1 = 10$  wt%. But at  $C_1 = 20$ –30 wt%, the  $G'$  values after cooling were single linear functions of AC, suggesting the feasibility of interpreting the elasticity of reconstituted starch systems after retrogradation by using weight-average AC. Generally, storage moduli of the starch blends after complete gelatinization and retrogradation followed isostress rules in a diluted



**Fig. 9.** Changes in the observed  $G'_{\max}$  (upper figures),  $G'_{95}$  (middle figures), and  $G'_{25}$  (lower figures) data of starch suspensions prepared from KSS7, TCW70, and their blends with TCW70 composition (% of total starch concentrations examined). Theoretical tendencies based on simplified isostress (dotted lines) and isostrain (solid lines) blending laws for composites without interactions between continuous and dispersed phases are given for comparison.

system ( $C_t = 10$  wt%) and were intermediate between isostress and isostrain rules for more concentrated systems ( $C_t = 20\text{--}30$  wt%), implying the structural changes from one of the weak matrices dispersed with strong fillers to one of the stronger matrices caused by increased starch concentration. More information about the effects of molecular structure, granular architecture, and water plasticization as well as AC on changing the thermal and rheological or mechanical properties of starch blends needs to be investigated using more diverse blends of starches or flours.

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