

# Evaluation of Compatibility of Rice Starch and Pectins by Glass Transition and Sub- $T_g$ Endotherms and the Effect of Compatibility on Gel Viscosity and Water Loss

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ABSTRACT

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Differences in molecular structure and hydrophilicity may affect the compatibility of food components in a highly concentrated solution. Mixtures of TNU519 rice starch (RS) and pectins with three different degrees of esterification (22, 64, and 92%) were used as a model system to evaluate the components' compatibility in a low-moisture system. When analyzed individually by differential scanning calorimetry (DSC), RS, low methoxyl pectin (LMP), intermediate methoxyl pectin (IMP), and high methoxyl pectin (HMP) showed the presence of a glass transition temperature ( $T_g$ ) at 75.2, 96.2, 96.4, and 93.5°C, respectively. Among mixtures, the compatible RS-HMP exhibited only a single  $T_g$  between the  $T_g$  values of the two components, whereas the incompatible RS-LMP showed two  $T_g$  values that were close to those of the individual components. The sub- $T_g$  endotherms of all three mixtures (1:1) were lower

than the means of the corresponding components. The degree of decrease was more pronounced in the RS-HMP mixture than in the others. The above results imply that the interaction, which led to close contact between side chains of the two components, was more intense in the compatible RS-HMP mixture than in the RS-IMP and RS-LMP mixtures. The decrease of the sub- $T_g$  endotherm can be used as an index to evaluate the degree of compatibility as well as the interaction occurring between the two molecules. The above findings were further verified by dynamic mechanical analyses. Both viscosity and water retention of the compatible RS-HMP mixed gel were significantly higher than those of the RS-IMP and RS-LMP mixed gels. This evidence further suggests that RS and HMP are compatible and exhibit a strong intermolecular interaction that increases gel viscosity and decreases water loss during high-temperature heating.

Starch is a semicrystalline polymer. During cooling, gelatinized starch can form a three-dimensional gel network within which the swollen starch granules are interspersed in a continuous amylose gel phase (Eliasson 1985, Imberty et al 1991). It is generally accepted that, if an appropriate starch concentration is used, both the continuous phase of amylose and the discontinuous phase of swollen granules and gelatinized amylopectin contribute to the gel properties. On the other hand, a high concentration of gelatinized starch may lead to retrogradation (or recrystallization) after long-term storage at low temperature (Miles et al 1985).

Both native starch granules and recrystallized starch molecules consist of a partially crystalline component (highly branched amylopectin) and an amorphous component (nearly linear amylose) (French 1984, Miles et al 1985). From a practical point of view, a perfectly crystalline polymer melts at a distinct temperature and undergoes a first-order transition. In contrast, an amorphous polymer in an immobilized glassy state becomes viscous, rubbery, and flexible at the glass transition temperature ( $T_g$ ) and undergoes a second-order-like transition upon heating (Levine and Slade 1988). This  $T_g$  reflects the major segmental (20–50 carbons) motions of the polymer backbone. The temperature location of  $T_g$  is affected by the presence of bulky side chains (Armeniades and Baer 1977) and the degree of crystallinity in a polymer (Slade and Levine 1987, Zeleznak and Hoseney 1987, Kalichevsky et al 1992). The segmental motion of the amorphous polymer is hindered by constraints imposed by forces within and between chains. Other factors affecting  $T_g$  are the thermal history of the material, molecular weight of the polymer, percentage of plasticizer, and miscibility of polymer blends (Levine and Slade 1988, Roos and Karel 1991, Liu and Leliever 1992, Thiewes and Steeneken 1997, Mizuno et al 1998). Other thermal relaxations such as  $\beta$ - and  $\gamma$ -transition can also be found below  $T_g$  of a low-moisture polymer. These low-temperature relaxations involve motions of relatively small groups around the backbone chains (Aklonis et al 1972, Kovarshii et al 1978). For instance, the  $\beta$ -transition is asso-

ciated with motion of side chains in a polymer (Aklonis et al 1972, Nielsen 1974). Starch, a semicrystalline polymer, may exhibit all of the above transitions.

Among the transition phenomena previously discussed,  $T_g$  of biopolymer mixtures is the most important parameter in understanding mechanical and storage properties of foods (Levine and Slade 1988). In general, compatible biopolymer mixtures show a single  $T_g$  between the  $T_g$  values of the two components if they are  $>20^\circ\text{C}$  apart. In contrast, incompatible mixtures will show two  $T_g$  values corresponding to the two individual components (Olabisi et al 1979, Kalichevsky and Blanshard 1992). Our study was based on the theory that changes in  $T_g$  are governed by the compatibility of two food components after mixing. Our goal was to use the thermal transition behavior ( $T_g$  and sub- $T_g$  endotherms) from differential scanning calorimetry (DSC) and dynamic mechanical analyses (DMA) as a probe to examine compatibility of TNU519 rice starch and pectins with various degrees of esterification (DE). The viscosity and the high-temperature water loss of mixed gels were also studied in this work. We also evaluated the relationship between compatibility and gel properties of rice starch and pectin.

## MATERIALS AND METHODS

### Rice Starch

Rice starch, indica (Tai-Nung Sen 19, TNU519) cultivar, was isolated from milled rice by a modified alkaline steeping method (Yang et al 1984). The starch was dried at 40°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 content was determined according to the method of Juliano et al (1981) using standard potato amylose and waxy rice starch (Tai-Chung Waxy 46) mixtures. Protein ( $N \times 6.25$ ) and lipid were analyzed according to the methods of Eliasson et al (1981).

### Preparation of Mixed Gel

Defatted TNU519 rice starch suspension (10%, w/w) was first partially gelatinized at 85°C with constantly stirring and then completely gelatinized at 110°C for 15 min in a pressure cooker without stirring. After cooling to 60°C, the gelatinized starch was mixed with low methoxyl pectin (LMP, 22% DE), intermediate methoxyl pectin (IMP, 64% DE), or high methoxyl pectin (HMP, 92% DE) at a 1:1 ratio and stirred at 60°C for 30 min. On a dry weight basis of gel-

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atinized starch, 10% (w/w) pectins was used for DSC and DMA, and 1% (w/w) pectins for viscosity and water loss measurements. Each mixture was slowly cooled to room temperature to form a gel.

For DSC and DMA, the gels were immediately freeze-dried and equilibrated with a saturated magnesium nitrate solution ( $a_w = 0.54$ ) in a closed container at room temperature for approximately five days to adjust the moisture content of each sample to  $14.0 \pm 0.5\%$ .

### Calorimetry

The thermal properties of the starch mixtures were examined using a differential scanning calorimeter (model 910, DuPont, Wilmington, DE) with a model 2100 thermal analysis data station. Sample ( $\approx 8.0$  mg) was hermetically sealed in a coated aluminum pan. A sealed empty pan was used as a reference. The sample was heated from 25 to 125°C at 10°C/min, held at 125°C for 30 min, and then cooled to room temperature before rescanning to 125°C at 10°C/min. The  $T_g$  and sub- $T_g$  endotherms of the characteristic transitions were recorded (Shogren 1992). After the DSC cell was heated to 550°C for cleaning, the instrument was calibrated with indium (onset = 156.6°C and enthalpy = 28.45 J/g) by heating from 25 to 200°C at 10°C/min. A maximum deviation in onset temperature of  $\pm 0.1^\circ\text{C}$  was allowed. All the DSC experiments were made at least in triplicate.

### DMA

The freeze-dried and moisture-equilibrated samples were cut with a die into a 20- × 5- × 20-mm rectangle and placed in a steel mold. Then they were pressed (100 kg/cm<sup>2</sup>) for 30 min to 10% of the original height (2 mm). Moisture-equilibrated samples were then analyzed using the three-point bending mode of a DMA-7e (Perkin Elmer, Norwalk, CT) at a frequency of 1 Hz. The analysis was performed from 20 to 140°C. A high heating rate of 10°C/min was used to avoid rapid moisture loss during heating which could greatly affect the transitions. The resultant storage modulus ( $E'$ ) and  $\tan\delta$  were recorded.

### Viscosity

Triplicate starch (5%, w/w) or mixed gel samples (10:1 starch to pectin) were prepared as previously described. Formation of gas bubbles in the gel was avoided during mixing; if necessary, a subsequent degassing step was done by centrifuging ( $3,000 \times g$ ) for 10 min. Before the viscosity test at  $25.0 \pm 0.5^\circ\text{C}$ , the gel was carefully transferred into a tilted beaker without generating gas bubbles.

A viscometer (LVF, Brookfield Engineering Laboratories, Stoughton, MA) was used to measure shear parameters. A single spindle was used for each measurement. The power-law model representing the relationship between shear stress and shear rate for non-Newtonian fluids is:

$$\tau_w = B(\dot{\gamma}_w)^n$$

where:  $\tau_w$  = shear stress at the wall (dyne/cm<sup>2</sup>);  $\dot{\gamma}_w$  = shear rate at the wall (1/sec);  $B$  = fluid consistency index.

For a non-Newtonian fluid, an apparent viscosity ( $\eta_{app}$ ) can be calculated as  $B(\dot{\gamma}_w)^{n-1}$ . Fluid consistency ( $B$ ) and flow behavior ( $n$ ) indices were obtained from a log-log plot of the equation:

$$\log(\tau_w) = \log(B) + n \log(\dot{\gamma}_w)$$

### Water Loss Analyses

Triplicate samples (5 g) of starch (5%, w/w) or mixed gel (5.5%, w/w, 10:1 starch-to-pectin ratio) were put in an aluminum pan ( $\approx 3$  cm diam) and placed in a hot-air oven at 160°C. The temperature of the gel rose to  $95.5 \pm 0.5^\circ\text{C}$  after 10 min of heating and remained at  $99.5 \pm 0.5^\circ\text{C}$  during 15–25 min of heating. Thus, the mixed gel samples were taken out of the oven after 10 and 20 min of heating. The samples were quickly covered and cooled in a closed container. The final weight of each sample was determined and the percentage of water loss was calculated from the weight loss.

### Statistical Analyses

Analysis of variance and comparisons among treatments were conducted on the data for thermal behavior, viscosity, and water loss (SAS Institute, Cary, NC). After a preliminary  $F$ -test, the differences among treatments were determined by Duncan's multiple range test at a 5% probability level.

## RESULTS AND DISCUSSION

### Composition of RS

The chemical composition of the TNU519 RS was 8.65% moisture content, 0.75% crude proteins, and 0.16% crude lipids. The trace amount of remaining lipids is mainly bound fatty acids and phospholipids in the RS (Kitahara et al 1997). The amylose content of RS was 23.6% (w/w).

### Thermal Properties

Starch gels prepared at  $\geq 94^\circ\text{C}$  may consist of a complex mixture of swollen granules, granule fragments, solubilized starch, and retrograded starch (Christianson and Bagley 1990). This is because leached amylose, on cooling, can form a gel network with cross-links resulting from chain interactions and entanglements. Swollen granules and granule fragments, in turn, may serve as fillers of the amylose network (Eliasson 1985, Imberty et al 1991). Swollen granules with little soluble leached amylose could also agglomerate to provide a weak gel. According to the study by Christianson and Bagley (1990), starch granules were highly swollen at 121°C for 30 min but still retained granule identity under static conditions. However, rice starch gel cannot be formed from samples prepared at 121°C under high shear because swollen granules may have been broken down and solubilized. When measured at 25°C in our study, gel viscosities of RS (5%, w/w) prepared by heating for 15 min at 95 and 110°C were not significantly different over the shear rate range of  $-0.5$  to  $0.5/\text{sec}$  (data not shown). Thus the partially gelatinized rice starch (10%, w/w) was then completely gelatinized

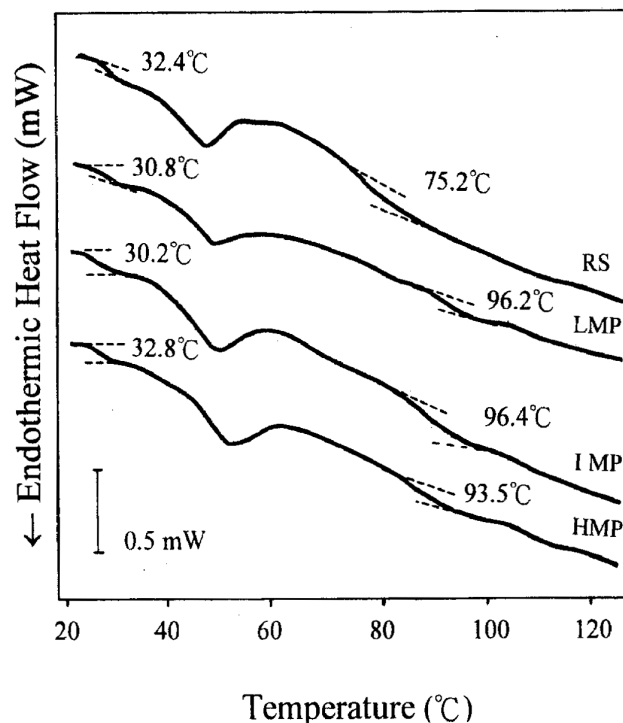


Fig. 1. Differential scanning calorimetry (DSC) profiles for TNU519 rice starch (RS) and pectins with  $14 \pm 0.5\%$  moisture content. LMP = low methoxyl pectin, IMP = intermediate methoxyl pectin, HMP = high methoxyl pectin.

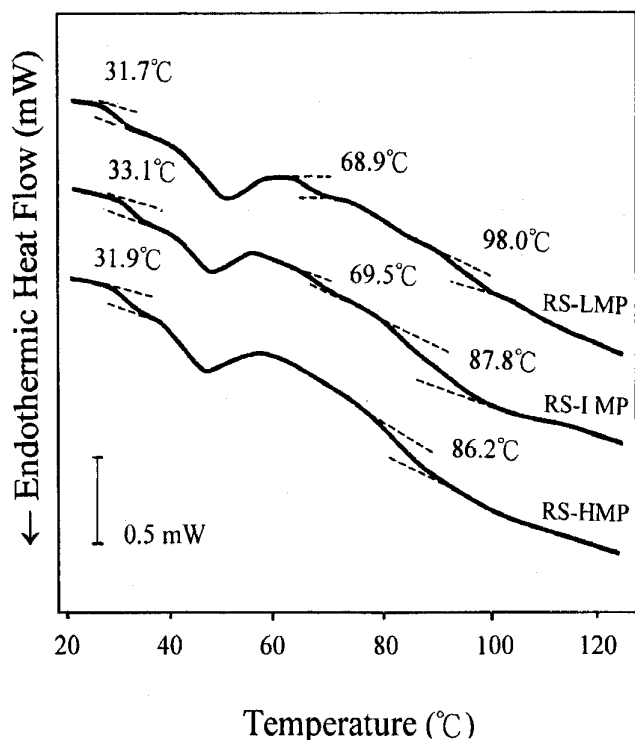
at 110°C for 15 min without stirring to obtain a fully swollen granules; this could lead to a large amount of leaked amylose from the granules.

It is well known that starch gels are nonequilibrium systems (Slade and Levine 1987, Biliaderis and Juliano 1993). Recrystallization of starch gel on storage reflects contributions from diffusion-controlled chain-folding processes (Biliaderis 1992). This self-association phenomenon (retrogradation) should be avoided because it will affect the intermolecular interaction of starch and other components (Miles et al 1985) and the resulting  $T_g$  (Zeleznaek and Hosney 1987). To study the interaction and compatibility between starch and pectins in an aqueous solution, all the samples for DSC and DMA analyses were immediately frozen with dry ice after preparation and cooling to room temperature.

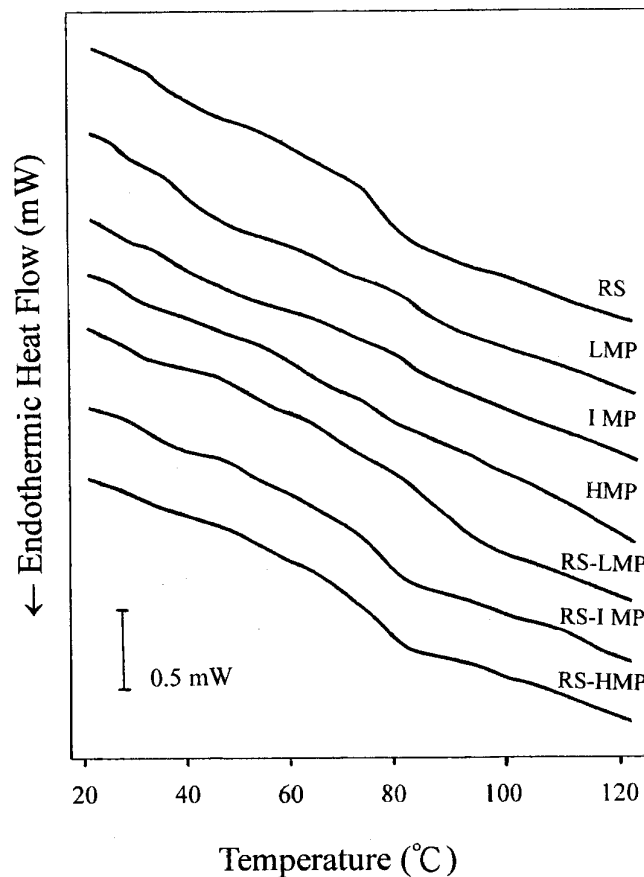
DSC scans of RS, pectins, and their mixtures are shown in Figs. 1 and 2, respectively. The higher temperature transition (baseline shift) was inversely related to moisture content, whereas the lower temperature transition (below the endothermic peak) was relatively insensitive (data not shown). Upon immediate rescanning, the high and low temperature transitions were recovered, while the endothermic peaks following the low temperature transitions were not (Fig. 3). These results are consistent with previous studies of aged amylopectin (Kalichevsky et al 1992, Appelqvist et al 1993). It appears that the high-temperature transition is the so-called glass transition temperature ( $T_g$ ). DSC results indicated that RS, LMP, IMP, and HMP had  $T_g$  values of 75.2, 96.2, 96.4, and 93.5°C, respectively (Fig. 1). Because the  $T_g$  values of RS and pectins were  $\approx 20^\circ\text{C}$  apart, the two components were suitable for a compatibility study (Olabisi et al 1979, Kalichevsky and Blanshard 1992). Also pectins with different DE carry different charges and may manifest different extents of hydration in a moisture-limited condition. The hydrophilicity is in the order: LMP > IMP > HMP. Our main purpose was to evaluate compatibility using RS and pectins as a model system in our study.

For the RS-LMP mixture,  $T_g$  values appeared at 68.9 and 98.0°C, which were close (within 2–6°C) to the  $T_g$  values for the individual components (Fig. 2). Hartley et al (1995) reported that the amount of water associated with starch in a mixture at a particular  $a_w$  is less than that for starch alone. Therefore, the slight difference in  $T_g$  may be due to a redistribution of water between the phases. According to Kalichevsky and Blanshard (1992), RS and LMP were incompatible because the individual components  $T_g$  values were still exhibited by the mixture. In addition to the  $T_g$  at 69.5°C which was close to the  $T_g$  of RS, a broad transition with  $T_g$  at 87.8°C was observed for the RS-IMP mixture. The evidence for a newly generated  $T_g$  and the disappearance of the original  $T_g$  for IMP at 96.4°C in the mixture indicated that partial compatibility may exist between RS and IMP. As for the RS-HMP mixture, only a single  $T_g$  was found which was located between the  $T_g$  values for the two individual components (Fig. 2). In previous studies (Olabisi et al 1979, Kalichevsky and Blanshard 1992), we concluded that HMP and RS are compatible, and the degree of compatibility of pectins with RS is in the order: HMP > IMP > LMP.

Both pectins (Aspinall et al 1968, Voragen et al 1986) and starch components, amylose and amylopectin (Biliaderis et al 1981, Manners et al 1989, Crua et al 1995), contain branches. The low-temperature relaxation ( $\beta$ -transition) which is associated with the motion of side chains should be found below  $T_g$  at low moisture content (Aklonis et al 1972, Nielsen 1974). On the other hand, when starch at 10–20% moisture is aged at a temperature below  $T_g$  for a certain amount of time, it will reveal a sub- $T_g$  endotherm (Shogren 1992). It has been suggested that this sub- $T_g$  relaxation process occurs between  $T_g$  and the  $\beta$ -transition temperature (Thiewes and



**Fig. 2.** Differential scanning calorimetry (DSC) profiles for TNuS19 rice starch (RS) and pectin mixtures (1:1) with  $14 \pm 0.5\%$  moisture content. LMP = low methoxyl pectin, IMP = intermediate methoxyl pectin, HMP = high methoxyl pectin.



**Fig. 3.** Immediate differential scanning calorimetry (DSC) rescans for samples shown in Figs. 1 and 2. RS = TNuS19 rice starch, LMP = low methoxyl pectin, IMP = intermediate methoxyl pectin, HMP = high methoxyl pectin.

Steeneken 1997). Due to the sensitivity of our DSC analyses, clearly discernible sub- $T_g$  transitions, instead of  $\beta$ -transitions (verified from DMA analyses), were observed at the leading edge of the endothermic peaks for all the samples: RS, pectins (Fig. 1), and mixtures (Fig. 2). In our DSC data, it was interesting to note that all the sub- $T_g$  values were not significantly different ( $\pm 2^\circ\text{C}$ ) (Table I). In contrast to those sub- $T_g$  results, the sub- $T_g$  endotherms were significantly different among samples. Moreover, they were not observed on rescanning (Fig. 3). The above results were consistent with previous calorimetric studies on starches (Shogren 1992, Appelqvist et al 1993, Yuan and Thompson 1994, Thiewes and Steeneken 1997).

If one further examined the data for the sub- $T_g$  endotherms, it could be seen that the sub- $T_g$  endotherms for the mixtures (sub- $T_g \Delta H_{RS-P}$ ) were smaller than the mean values of the corresponding components ( $1/2[\text{sub-}T_g \Delta H_{RS} + T_g \Delta H_P]$ ) for all three mixtures (Table I). It is also notable that the reductions of the sub- $T_g$  endotherms in the RS-HMP and RS-IMP mixtures were more pronounced than in the RS-LMP mixture.

Up to now, the explanations given for sub- $T_g$  endotherms have been ambiguous and are still a matter of much debate. However, two agreed-upon features of these sub- $T_g$  endothermic peaks are that they appear on storage for starch with limited moisture content (Kalichevsky et al 1992, Shogren 1992, Appelqvist et al 1993), and these endotherms increase with increases in moisture content (Shogren 1992, Appelqvist et al 1993). Based on results from CP/MAS  $C^{13}$  NMR spectra, Shogren (1992) concluded that the sub- $T_g$  endotherm observed in starch is not due to the melting of a helix or other highly organized structure. The two main explanations for the sub- $T_g$  endotherm reported for starch are enthalpy relaxation (Shogren 1992, Thiewes and Steeneken 1997) and carbohydrate-water interactions (Appelqvist et al 1993, Yuan and Thompson 1994). Although the nature of the starch-pectin interaction remains obscure, it is possible that interaction, resulting from compatibility of the two molecules, would lead to close contact of the two molecules, especially at the outermost branches and thus result in the decrease of the sub- $T_g$  endotherm observed in the mixture. This is because the decrease of the sub- $T_g$  endotherm of the two compatible molecules might reflect steric hindrance of enthalpy relaxation under conditions of restricted relaxation toward lower enthalpy (enthalpy relaxation) or inhibition of the energetic association of water and the hydrophilic side chains of either polymeric molecule (carbohydrate-water interactions). If this were true, one would expect that the decrease in the sub- $T_g$  endotherm for the compatible RS-HMP mixture, which is due to the miscibility of the two components and to reorientation of their side chains, would be more pronounced than that for the RS-LMP mixture. In other words, the above finding revealed that the decrease of the sub- $T_g$  endotherm could be used as an index to evaluate the degree of compatibility, as well as interaction, occurring between the two molecules. These phenomena are consistent with the theory of

**TABLE I**  
Glass Transition Temperatures ( $T_g$ ) and Sub- $T_g$  Endotherms of 1:1 Mixtures of TNU19 Rice Starch (RS) and Pectin with  $14 \pm 0.5\%$  Moisture Content

Sample <sup>a</sup>	Sub- $T_g$ ( $^\circ\text{C}$ )	Sub- $T_g \Delta H$ (J/g)	$T_{g(\text{low})}$ ( $^\circ\text{C}$ )	$T_{g(\text{high})}$ ( $^\circ\text{C}$ )
RS	$32.4 \pm 0.3a^b$	$0.85 \pm 0.01a$	$75.2 \pm 0.8a$	nd <sup>c</sup>
LMP	$30.8 \pm 1.9a$	$0.57 \pm 0.02e$	nd	$96.2 \pm 0.6b$
IMP	$30.2 \pm 1.3a$	$0.79 \pm 0.06ab$	nd	$96.4 \pm 0.2b$
HMP	$32.8 \pm 0.4a$	$0.72 \pm 0.08bc$	nd	$93.5 \pm 0.3c$
RS-LMP	$31.7 \pm 2.4a$	$0.69 \pm 0.04cd$	$68.9 \pm 0.6b$	$98.0 \pm 0.7a$
RS-IMP	$33.1 \pm 1.8a$	$0.67 \pm 0.01cd$	$69.5 \pm 0.6b$	$87.8 \pm 1.0d$
RS-HMP	$31.9 \pm 1.5a$	$0.63 \pm 0.03de$	nd	$86.2 \pm 1.2e$

<sup>a</sup> LMP = low methoxyl pectin, IMP = intermediate methoxyl pectin, HMP = high methoxyl pectin.

<sup>b</sup> Means of triplicates values followed by the same letter in the same column are not significantly different ( $P < 0.05$ ).

<sup>c</sup> Not detected.

Smith and Boyd (1992), who pointed out that reorientation of flexible side chains might be the underlying cause of a sub- $T_g$  relaxation.

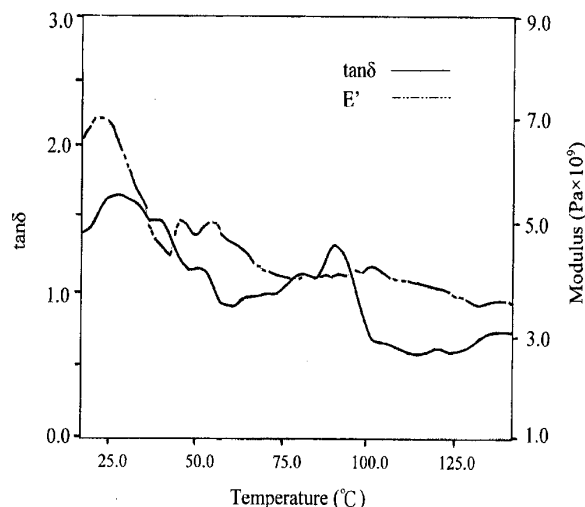
## DMA

Although DSC has been most commonly used to detect first-order (melting) and second-order-like transitions ( $T_g$ ), DMA is preferred over DSC, especially for measurements of  $T_g$ , because it is far more sensitive ( $>1,000\times$ ) (Rotter and Ishida 1992, Wetton 1986), and because it also monitors rheological properties. DMA also provides further insight into segmental movement within a gel network at a low moisture content. It demonstrates mechanical responses that reflect the magnitude of energy stored ( $E'$ , storage modulus) and energy dissipated ( $E''$ , loss modulus) in a gel structure and that signify the relaxation of different amorphous chains. Therefore, the  $\tan\delta$  ( $E''/E'$ ) is often used at a given frequency to describe  $\alpha$ -( $T_g$ ),  $\beta$ -, and  $\gamma$ -transitions.

Changes in  $\tan\delta$  peak amplitude at 1 Hz may vary with composition and are very dependent on moisture content of a sample (Kalichevsky et al 1992, Vodovotz and Chinachoti 1996). To avoid having the transitions occur around the ice melting region, samples with  $14 \pm 0.5\%$  moisture content were used in this study. However, at 14% moisture, a small  $E'$  may occur over a wide temperature range, and transitions become less distinct (Vodovotz and Chinachoti 1996). Also, a broadening of the transition suggests possible multiple transitions, which have been attributed to an increase in the heterogeneity of segmental mobility in starch (Vodovotz et al 1996). Thus,  $T_g$  was investigated in this study by observing  $E'$  and  $\tan\delta$  as functions of temperature, and was defined as a peak in  $\tan\delta$  within the decreasing range of  $E'$ , in accordance with Kalichevsky et al (1992).

$E'$  and  $\tan\delta$  as functions of temperature for RS are plotted in Fig. 4. Above  $25^\circ\text{C}$ , the sample exhibits a sharp decrease in  $E'$ , with  $\tan\delta$  peaks at 35, 40, 51, 80, and  $88^\circ\text{C}$ . According to a study by Kalichevsky et al (1992), there can be a difference of  $\approx 10$ – $20^\circ\text{C}$  between the  $T_g$  values analyzed by DSC and DMA. If this were so for our DMA data, the  $\tan\delta$  peaks at 51 and  $88^\circ\text{C}$  were the sub- $T_g$  and  $T_g$  transitions, respectively, in comparison to the DSC data.

Up to this point, we had no evidence whatsoever that directly supported the presence of the  $\tan\delta$  peaks at 35, 40, and  $80^\circ\text{C}$ . However, it is interesting to note that the heights of the  $\tan\delta$  peaks at 35 and  $40^\circ\text{C}$  were much higher than that at  $51^\circ\text{C}$  (Fig. 4). Our RS samples contained 76.4% (w/w) of highly branched amylopectin, and they should have exhibited a strong  $\beta$ -transition signifying the relax-



**Fig. 4.** Dynamic mechanical analyses (DMA) plot for TNU19 rice starch with  $14 \pm 0.5\%$  moisture content.

ation of side chains in the polymer (Aklonis et al 1972, Nielsen 1974). Because the height of the  $\tan\delta$  peak is related to the volume of the relaxing phase (Wetton 1986), the transitions at 35 and 40°C appear to be  $\beta$ -transitions that are normally found at temperatures below  $T_g$ . Although we have no definitive explanation for the  $\tan\delta$  peak at 80°C, which is small and very close to the  $T_g$ , it may represent a the relaxation of minor domains of the amorphous starch.

Figure 5 shows the DMA plot for HMP. Similarly,  $\tan\delta$  peaks at 60 and 118°C indicate sub- $T_g$  and  $T_g$  transitions for HMP, respectively. In light of the highly branched L-rhamnopyranose and galacturonosyl backbone residues of pectins (De Vries et al 1983, Renard et al 1991), the  $\tan\delta$  peak at 45°C might be the  $\beta$ -transition of those side chains (Fig. 5). As for starch, the  $\tan\delta$  peaks at 80 and 95°C for HMP might also be the transitions of minor amorphous domains. For the RS-HMP mixture, peaks at 45 and 60°C, possibly representing  $\beta$ - and sub- $T_g$  transitions, still appear in Fig. 6, but with lower peak heights. Also observed in Fig. 6 were two transitions of minor amorphous domains at 77 and 97°C, possibly shifted from 80 and 95°C for HMP. Unlike the DSC data, a clear  $T_g$  peak at 118°C for HMP still existed in the mixture. However, a new  $T_g$  peak appeared at  $\approx 105^\circ\text{C}$ , and the  $T_g$  at 88°C for RS was no longer observed in the mixture (Fig. 6). It is interesting to note that the  $\tan\delta$  peak height at 118°C for the RS-HMP mixture was lower than that for HMP. This implies that the volume of the relaxing phase, resulting from the mobility of amorphous backbone, was less in the mixture than in HMP alone. According to previous studies (Olabisi et al 1979, Wetton 1986, Kalichevsky and Blanshard 1992), the evidence revealed from the DMA data indicates that the RS and HMP molecules in the gel were somewhat compatible. The appearance of HMP  $T_g$  (118°C) in the mixture indicates that the mixing ratio of 1:1 was not optimally chosen in our study. The excess amount of HMP (not involved in the gel network with RS) exhibited its  $T_g$  in the RS-HMP mixture when analyzed by DMA.

### Viscosity

Gel structure and the intermolecular interactions existing between starch and food gums are commonly evaluated on the basis of rheological properties (Sudkakar et al 1995). Starch gel formation, resulting from thermodynamic incompatibility, produces a two-phase system at high water content. With decreasing water content, phase separation may be physically inhibited. According to a study by Kalichevsky and Ring (1987), the miscibility of linear and branched neutral polysaccharides is evidently limited in an amylose-amylopectin-water system. The above phenomena were further confirmed

by Yuryev et al (1995) in a phase-state study of starch gel. Thus, under certain conditions, a synergistic (due to compatibility) or adverse (due to phase separation) effect in a starch-hydrocolloid system can be visualized on a simple viscosity basis. This is because starch gelation is strongly influenced by the continuous gel phase of amylose (Eliasson 1985, Imberty et al 1991) and would be modified by the added hydrocolloid (Ellis and Ring 1985, Alloncle and Doublier 1991).

The gel viscosity of RS (5%, w/w) in the presence of pectins (0.5%, w/w) is shown in the absence of storage (Fig. 7) and after one day of storage (Fig. 8). The apparent viscosity ( $\eta_{app}$ ) can be calculated as  $B(\dot{\gamma}_w)^{n-1} \cdot \eta_{app}$  of 0.5% LMP, IMP, or HMP alone was  $<100$  cp in both studies (data not shown), and each line was close to the  $x$ -axis over the shear rate range of  $-0.5$  to  $0.5/\text{sec}$ . Therefore, the viscosity data for the three individual pectins were not shown in either figure. A synergistic effect was observed for the compatible RS-HMP mixed gel, for which  $\eta_{app}$  was up to 1.4 times (for no storage) or 1.6 times (for one day of storage) higher than that for RS (Figs. 7 and 8, Table II). On the other hand,  $\eta_{app}$  of the RS-IMP and RS-LMP mixed gels was lower than that of the RS gel. Viscosities were in the order: RS-HMP  $>$  RS  $>$  RS-IMP  $>$  RS-LMP. Gels after one day of storage showed a trend similar to those not stored (Fig. 8), except that the viscosities were in the order: RS-HMP  $>$  RS-IMP  $>$  RS  $>$  RS-LMP. The  $\eta_{app}$  of the mixed gels stored for one day was 2.9 to 3.4 times higher than that for the corresponding gels with no storage. We suggest that the reason for the synergistic effect on viscosity is that HMP molecules are neutral and readily come into close contact with amylose, in contrast to LMP molecules, which carry a high percentage of negative charges. Due to the high hydrophilicity of LMP molecules, they might gradually expel amylose molecules and disturb their gel formation during initial mixing in an aqueous solution. This result was consistent with a previous finding by Chien (1993).

The flow behavior indices ( $n$ ) of gels are listed in Table II. A higher  $n$  value, signifying a lower pseudoplasticity, reveals a stronger intermolecular interaction (Szczesniak 1977, Sajjan and Rao 1987). All the mixed gels, with or without storage, showed pseudoplastic behavior ( $0 < n < 1$ ). The decreases in  $n$  for all the gels, after storage for one day, might have been due to the incompatibility of amylose and amylopectin ( $n_{0\text{day}} > n_{1\text{day}}$ ) (Kalichevsky and Ring 1987). This negative effect on all the gels during storage was contradictory to the viscosity data. We have no definitive explanation

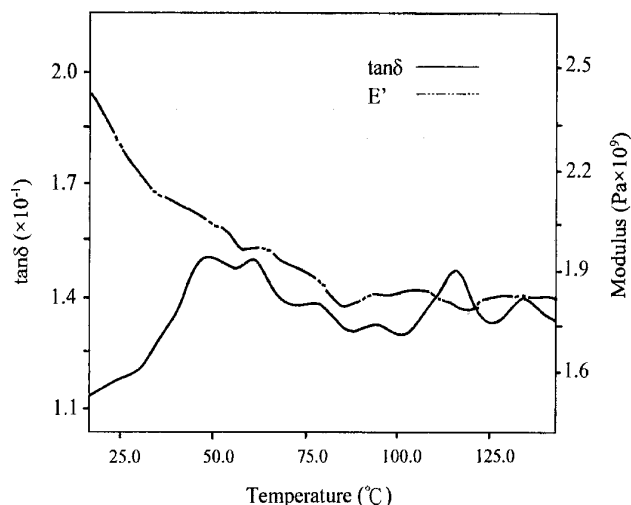


Fig. 5. Dynamic mechanical analyses (DMA) plot for high methoxyl pectin with  $14 \pm 0.5\%$  moisture content.

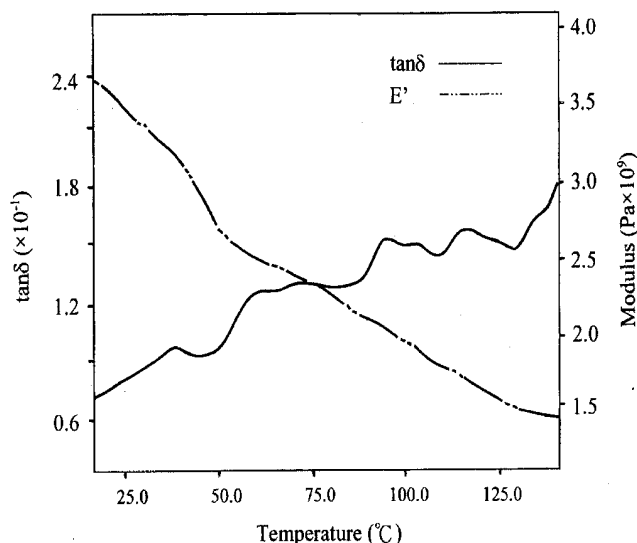
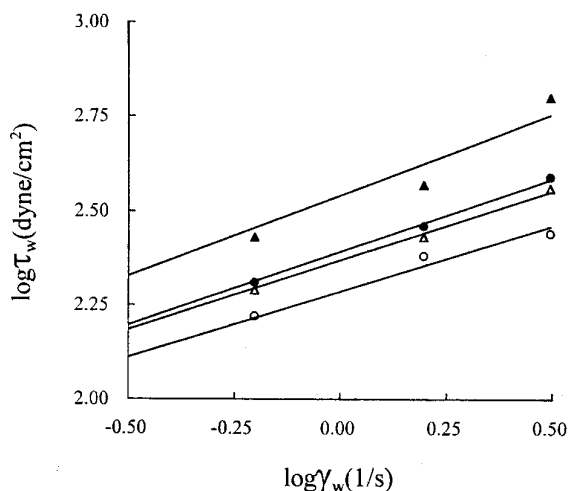


Fig. 6. Dynamic mechanical analyses (DMA) plot for 1:1 mixture of TNuS19 rice starch (RS) and high methoxyl pectin (HMP) with  $14 \pm 0.5\%$  moisture content.

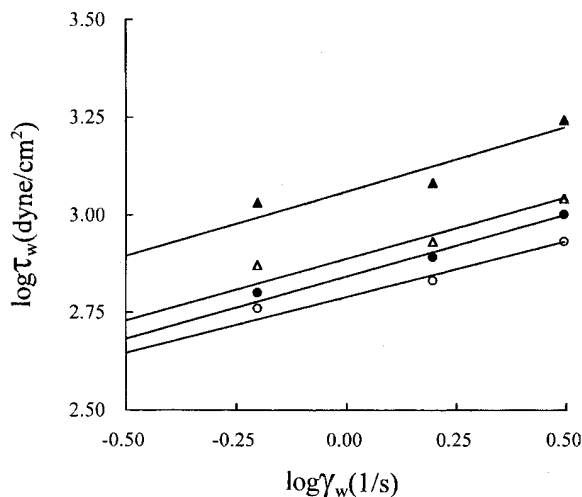
for this. However, we consider it compelling evidence that the RS-HMP mixed gel manifested stronger intermolecular interactions than did the RS-LMP mixed gel, since the  $n$  of the former was significantly higher than that of the latter (Table II). We can thus conclude that compatibility analyzed at low moisture content is positively correlated with the viscosity and  $n$  value of a gel formed in an aqueous solution.

### Water Loss

Water loss caused by a high-temperature dehydration process affects various physical and chemical characteristics of foods (Barbosa-Cánovas and Vega-Mercado 1996). Among the physical aspects, a decrease in viscosity at elevated temperature is commonly found for most food gels. Water loss measured at high temperature has been used as an index to evaluate the water retention of a gel during heating (Chien 1993). The percentage of water loss



**Fig. 7.** Effect of compatibility on the viscosity of TNuS19 rice starch (RS) and pectin mixed gels (10:1) with 5.5% solids content. Log shear stress ( $\tau_w$ ) versus log shear rate ( $\gamma_w$ ) was plotted for each sample. RS (●), RS and low methoxyl pectin (○), RS and intermediate methoxyl pectin (△), RS and high methoxyl pectin (▲).



**Fig. 8.** Effect of compatibility on viscosity of TNuS19 rice starch (RS) and pectin mixed gels (10:1) with 5.5% solids content after one day of storage at 25°C. Log shear stress ( $\tau_w$ ) vs. log shear rate ( $\gamma_w$ ) was plotted for each sample. RS (●), RS and low methoxyl pectin (○), RS and intermediate methoxyl pectin (△), RS and high methoxyl pectin (▲).

for all the mixed gels is listed in Table III. Water loss results indicated that the gels stored for one day had a greater tendency to lose water at elevated temperature than did those with no storage. For the gels without storage, the percentage of water loss after 10 or 20 min of heating followed the same order: RS-HMP < RS-IMP < RS < RS-LMP. After storing for one day, the gels heated for 20 min showed water loss in the order: RS-HMP < RS-IMP, RS < RS-LMP, which was similar to the order for the previous data. Synergism was still evident in that compatibility was positively correlated with water retention in the mixed gels.

### CONCLUSIONS

To evaluate the components' compatibility in a low-moisture system, TNuS19 rice starch (RS) and pectins with three different DE (LMP, IMP, and HMP) were used in this study. They all showed  $T_g$ . The compatible RS-HMP mixture exhibited only a single  $T_g$  between the  $T_g$  values of the two individual components, whereas the incompatible RS-LMP mixture showed two  $T_g$  values. From comparisons between the mixtures and the corresponding components, the degree of decrease in the sub- $T_g$  endotherm was more pronounced for the RS-HMP mixture than for the others. The interaction, suggested to have led to close contact between the two components' side chains, was more intense in the compatible RS-HMP mixture than in the other two mixtures. We suggested that the changes in  $T_g$  and sub- $T_g$  endotherm can be used to evaluate the degree of compatibility and the extent of interaction occurring between two molecules. Both viscosity and high-temperature water retention of the compatible RS-HMP mixed gel were significantly higher than those of the RS-IMP and RS-LMP mixed gels. This evidence further suggests that RS and HMP are compatible and undergo strong intermolecular interaction that results in an increase in gel viscosity and a decrease in water loss during high-temperature heating.

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**TABLE II**  
Fluid Consistency ( $B$ ) and Flow Behavior Indices ( $n$ ) for TNuS19 Rice Starch (RS) and Pectin Mixed Gels After Zero or One Day of Storage

Gel <sup>a</sup>	0 Day		1 Day	
	$B$	$n$	$B$	$n$
RS	244b <sup>b</sup>	0.39b	698b	0.31ab
RS-LMP	191a	0.35b	613a	0.28b
RS-IMP	230b	0.36b	772c	0.31ab
RS-HMP	345c	0.43a	1,122d	0.33a

<sup>a</sup> LMP = low methoxyl pectin, IMP = intermediate methoxyl pectin, HMP = high methoxyl pectin.

<sup>b</sup> Means of triplicates values followed by the same letter in the same column are not significantly different ( $P < 0.05$ ).

**TABLE III**  
Water Loss (% w/w) after 10 or 20 min of Heating TNuS19 Rice Starch (RS) and Pectin Mixed Gels After Zero or One Day of Storage

Gels <sup>a</sup>	0 Day		1 Day	
	10 min	20 min	10 min	20 min
RS	18.8 ± 1.2b <sup>b</sup>	39.2 ± 1.2b	20.1 ± 2.1b	45.9 ± 2.9b
RS-LMP	22.5 ± 1.0a	48.0 ± 1.0a	23.6 ± 2.6a	52.7 ± 2.4a
RS-IMP	16.4 ± 0.7c	35.5 ± 3.5c	22.5 ± 2.5ab	43.7 ± 1.9b
RS-HMP	13.5 ± 1.3d	25.8 ± 0.7d	20.1 ± 2.0b	38.9 ± 1.7c

<sup>a</sup> LMP = low methoxyl pectin, IMP = intermediate methoxyl pectin, HMP = high methoxyl pectin.

<sup>b</sup> Means of triplicates values followed by the same letter in the same column are not significantly different ( $P < 0.05$ ).

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