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Influence of Lipids on the Thermal and Mechanical Properties of Concentrated Starch Gels

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Interactions between lipids [sodium dodecyl sulfate (SDS); glycerol monostearate; cetyltrimethylammonium bromide; L-α-lysophosphatidylcholine (LPC)] and starches (wheat, rice, pea, and garbanzo bean) were studied in thermoset gel networks of high starch concentrations (20–35% w/w) by small amplitude oscillatory shear measurements and differential scanning calorimetry. All lipids reduced the apparent gelatinization enthalpies of the granular starches, suggesting complexation with the starch molecules upon heating; granule structure destabilization effects were shown only with SDS. Although rice and wheat starch gels exhibited higher storage modulus (G') values when lipids were included, smaller changes in the viscoelastic properties were observed for the legume starches; the higher amylose content of pea and garbanzo bean starches appears to dominate the rheological behavior of their composite gels. Among the lipids examined, LPC exerted the greatest effect in increasing the G' and decreasing the tan δ (G''/G') of rice and wheat starch gels. Kinetic experiments on the evolution of modulus (G') and the development of the staling endotherm during storage of gels (35% w/w, 8 °C) indicated that lipids retard both processes. At concentrations between 8 and 40% (w/w) of rice and garbanzo bean starch gels, the dependence of storage modulus on starch concentration (C) followed power law relationships; G' varied as $C^{2.1-2.9}$.

INTRODUCTION

Starch constitutes an excellent inert filler for modifying the texture of foodstuffs because of its thickening and gelling properties (Radley, 1976a). At high concentrations a three-dimensional solvated network is established when aqueous starch dispersions are heated and cooled. The gelation process involves mainly nonspecific interchain associations between starch molecules. In contrast to other entanglement polysaccharide network systems (e.g., pectins, marine hydrocolloids), which on a macroscale are homogeneous, starch gels are generally regarded as composite networks in which swollen starch granules are embedded in a continuous gel matrix phase (Ring and Stainsby, 1982; Ring, 1985). Consequently, the mechanical properties of starch gels are different from those of pure amylose and amylopectin gels; both the continuous phase (amylose matrix) and filler particles (gelatinized granules) contribute to the viscoelasticity. In this respect, granule size, chemical (amylose/amylopectin ratio) and physical constitution of the granule, minor starch components (granular lipids and phosphorus), and shear–temperature–time history are all important factors to the characteristics of starch gels (Radley, 1976b). Two recent comprehensive reviews have dealt with the factors affecting the rheological behavior of starch (Launay et al., 1986; Doublier, 1990).

Lipids have long been known to affect gelatinization and texture of starch-thickened foods. Monoacyl lipids form inclusion complexes with starch molecules, particularly with amylose (Krog, 1971), and it is likely that texture modification is primarily due to these interactions. However, the underlying mechanisms by which complex formation governs the thermal and mechanical properties of starch gels are far from clear. There appears to be a reduction in the pasting temperature (viscoamylography) of cereal starches after solvent extraction of the endogenous lipids (Goering et al., 1975; Melvin, 1979; Eliasson et al., 1981a; Takahashi and Seib, 1988); interestingly, this is not accompanied by changes in the characteristic melting temperatures, as assessed by calorimetry (Eliasson et al., 1981a; Takahashi and Seib, 1988). When present as adjuncts, monoacyl lipids reduce the gel volume and amylose leaching (Eliasson et al., 1981b; Hoover and Hadziyev, 1981; Eliasson, 1985). The extent and mode of interactions between granular starch and added lipids also depend on the nature of the lipid. Thus, while swelling and gelatinization are restricted with certain emulsifiers and fatty acids, addition of some ionic surfactants (e.g., SDS) promotes swelling of the granules (Harbitz, 1983; Gough et al., 1985; Eliasson, 1985). These effects and the resultant rheological behavior are modulated by the concentration of the various components, pH, presence of different salts, and heat–shear regime applied. This could explain the inconsistencies in the published data regarding the effects of lipids on starch rheology. Furthermore, most of the earlier reported work was carried out by using empirical rheological tests (e.g., Brabender viscoamylograph), where, due to the temperature–shear cycles employed, it is difficult to separate the impact of mechanical damage of the gel network from contributions of the lipid additive. Consequently, a whole gamut of effects has been observed, ranging from large increases in gel consistency, no effect, to large viscosity reductions (Goering et al., 1975; Melvin, 1979; Evans, 1986; Takahashi and Seib, 1988). Therefore, it is important to study the viscoelastic properties of starch gels under controlled conditions of thermal and mechanical treatments.

An additional effect of lipids is related to their antifirming action on processed starch-based foods (Krog, 1971). Following gelatinization, aqueous starch systems exist as metastable, nonequilibrium states which tend to undergo structure transformation during storage via chain aggregation and recrystallization (Miles et al., 1985a,b). These processes are believed to be responsible for the increased firmness (staling) of baked products (Kulp and Ponte, 1981). Although the molecular mechanisms are

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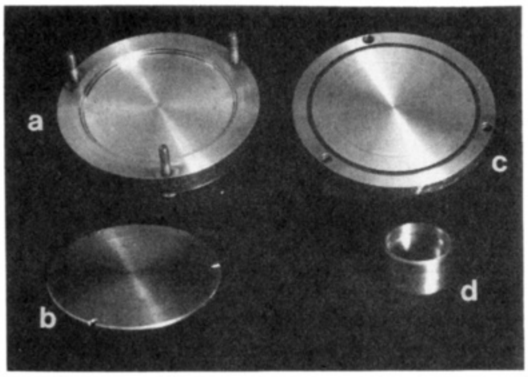

Figure 1. Hermetically sealed stainless steel disk used for casting starch gels: (a) bottom plate; (b) cover lid allowing 1-mm gap; (c) top plate with sealing O-ring; (d) gel cutting ring (30-mm diameter).

not well understood, lipid emulsifiers are known to have an antistaling influence on wheat bread and other bakery items.

The present study was undertaken to determine the effect of lipids (endogenous granular and added lipids) on the viscoelastic properties of thermoset starch gels using small-strain oscillatory rheological testing. Unlike most studies in the past on fairly dilute starch dispersions (<15% w/w) and under large deformations, the present work deals with the rheology of concentrated gels (20–35% w/w) to approach actual food product situations. The ability of lipids to interact with the starch as well as their antistaling action was probed by differential scanning calorimetry (DSC) and small deformation rheological measurements. It is hoped that such studies may lead to a better understanding of the underlying molecular interactions and the related macroscopic/sensory attributes observed when lipids are included in starch-based food formulations.

EXPERIMENTAL PROCEDURES

Materials. Commercial samples of wheat and pea starches were obtained from Ogilvie Mills (Midland, ON, Canada) and Protein Technologies International (St. Louis, MO), respectively. Rice starch was provided by the International Rice Research Institute (Manila, Philippines), while garbanzo bean (*Cicer arietinum*) starch was prepared by a wet-milling process according to the procedure of Biliaderis et al. (1979). Glycerol monostearate (GMS) was a product of Eastman Kodak Chemicals (Rochester, NY), while L-α-lysophosphatidylcholine (LPC) and cetyltrimethylammonium bromide (CTAB) were products of Sigma Chemical Co. (St. Louis, MO). Sodium dodecyl sulfate (SDS) was obtained from Bio-Rad Laboratories (Richmond, CA). All other reagents were of analytical grade. Rice and wheat starches were defatted by extraction with 85% methanol (4 h). Starch was assayed by a dual-enzyme method using α-amylase (Tenase, Miles Laboratories, Elkhart, IN), glucoamylase (Diazyme L-200, Miles), and glucose oxidase–peroxidase–4-aminoantipyrine (dye) enzyme system (Biliaderis et al., 1981). Amylose contents were determined by potentiometric titration (Schoch, 1964). Average granule size was determined by measuring 200 granules on photomicrographs (300× magnification) taken with a Carl Zeiss research microscope.

Preparation of Starch Gels. Starch gels were prepared by heating starch slurries of the appropriate starch concentration in a hermetically sealed stainless steel container (Figure 1; disk dimensions 80 mm i.d. × 1 mm thickness). The disk was immersed in a boiling water bath (15 min) and subsequently quench-cooled in a water bath at 25 °C (15 min). Rheological measurements were made immediately after gelation to avoid complications arising from gel structure modification due to retrogradation. Using this device, 1 mm thick gels were cast without loss of water and mechanical damage of the network. Gel disks with a diameter of 30 mm were cut to fit the parallel plate geometry of the rheometer. Composite starch gels with lipids were prepared by first dissolving the additive in water and then adding the granular starch. Because of its water insolubility, GMS was first dissolved in 95% ethanol and impregnated with the granules; the ethanol was removed under vacuum at 60 °C. All lipids were added at a 2 or 4% level on a dry starch weight basis.

Rheological Measurements. The mechanical properties of starch gels were monitored by small amplitude oscillatory testing using a Bohlin VOR rheometer (Bohlin Rheologi Inc., Edison, NJ), operated with a parallel plate geometry (30-mm diameter) and a torque element of 93.2 g·cm. Measurements were conducted at 25 °C in a frequency range of 0.1–20.0 Hz. The kinetic aspects of gel structure development (storage at 8 °C) of 35% (w/w) starch gels were probed at 0.2 Hz and strain less than 1.4%; data were collected at 30-min intervals for 16 h. In these experiments, a thin layer of paraffin oil was used to cover the sample and thus prevent water losses due to evaporation (Biliaderis and Zawistowski, 1990). Preliminary experiments indicated negligible contributions to the rheological parameters from the oil itself, while no oil migration was seen between the plate and the sample disk. All dynamic measurements were performed at lower than 2% strain, a range within the linear viscoelastic regime. Data comparisons among samples were made by using the values associated with a particular frequency. The dynamic rheological parameters used to evaluate the gels were the storage modulus (G'), dynamic viscosity ($\eta' = G''/2\pi f$, where G'' is the loss modulus and f the frequency), and tan δ or loss tangent ($\tan\delta = G''/G'$). The latter parameter represents the ratio of energy lost to the energy stored per each cycle of deformation and is a useful indicator of the relative contributions of the viscous (G'') and elastic (G') components to the viscoelastic properties of a material. The rate of G' development for the time-dependent studies was estimated by applying a first-order reaction kinetic model

$$kt = \log (G'_{\mathrm{c}} - G'_0/G'_{\mathrm{c}} - G'_t)$$

where G'_0, G'_t, and G'_{c} are the modulus values at time zero, t, and the completion of the experiment, respectively, while k is the apparent rate constant and t is time in minutes; for this kinetic analysis G' data between 2 and 16 h were used.

DSC Measurements. Differential scanning calorimetry of granular starches and gels was carried out by using a Du Pont 9900 thermal analyzer equipped with a 910 DSC pressure cell. Starch samples (3.6–3.8 mg) were suspended in water or aqueous solutions of lipids at 35% (w/w) solids and hermetically sealed in DSC pans. To determine the effect of lipids on starch recrystallization (staling), the starch suspensions were first heated to 135 °C (10 °C/min) to gelatinize the granules under constant pressure (1400 kPa with N_2), cooled to room temperature, and then stored for a designated period of time (4, 24, 48, and 96 h) at 6 °C before DSC analysis of the staling endotherm. All other conditions for calibration and operation of the calorimeter were as described previously (Biliaderis et al., 1985).

Statistical Analysis. Analysis of variance was carried out on the thermal and rheological data, and differences among samples were determined by Duncan's multiple range test.

RESULTS AND DISCUSSION

Starch Properties and Precision of Rheological Measurements. The composition and properties of granular starches used in this study are given in Table I; a broad range in physical and chemical properties was found among the starches. Starch content assays gave values greater than 93.8% in all cases. With respect to factors known to affect starch rheology, it is important to point out the higher amylose content and granule size of the legume (pea and garbanzo bean) starches, compared to their cereal (rice and wheat) counterparts, as well as the lack of endogenous lipids from legume starches. It is also worthy to note the higher gelatinization enthalpy of rice starch (13.8 J g^{-1}), a sample prepared under mild extraction conditions. The much lower enthalpy values obtained for the other starches (ΔH = 4.3–6.3 J g^{-1}) are indicative of granular order loss during the isolation of these materials.

Table I. Composition and Some Physical Properties of Cereal and Legume Starches

	starch content,[a] %	amylose content,[b] %	DSC characteristics[c] peak temp, °C	DSC characteristics[c] enthalpy, J g^{-1}	granule size[d] width–length, µm	lipids, %
wheat	98.9 ± 0.1	23.8 ± 0.4	57.4 ± 0.1	6.3 ± 0.1	2–8 (spherical), 18–24 (lenticular)	0.64
rice	96.3 ± 0.7	21.3 ± 0.1	73.2 ± 0.2	13.8 ± 0.1	4–9	0.82
pea	93.8 ± 1.8	32.7 ± 1.0	59.2 ± 0.3	4.3 ± 0.3	19–28	0.01
garbanzo bean	96.4 ± 0.1	31.2 ± 0.4	66.1 ± 0.2	6.2 ± 0.3	18–24	0.03

[a] Means ±SD (n = 3). [b] Based on starch content. [c] DSC data on 35% (w/w) starch dispersions. [d] Average values of 200 granules.

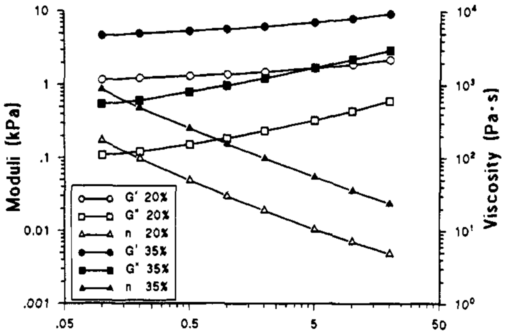

Figure 2. Frequency dependence of dynamic moduli (G' and G'') and viscosity (η') of wheat starch gels (20 and 35%) at 25 °C.

Shear, although absent in most thermal processing operations of starch-containing foods (e.g., baking), is an important determinant of the viscoelastic behavior of granular starch dispersions (Launay et al., 1986). In the present investigations, gels were quickly set (at 98–100 °C) from aqueous suspensions of granules by using the apparatus in Figure 1 under static conditions (no shear). The frequency dependence of the dynamic moduli (G', G'') and dynamic viscosity (η') of wheat starch gels at 20 and 35% (w/w) concentration is shown in Figure 2. These plots, known as mechanical spectra, give valuable information about the nature of the network. For all starch gels, over the frequency range 0.1–20.0 Hz, G' and G'' exhibited very little frequency dependence. This behavior is typical of a "true" gel (with permanent cross-links) rather than an entanglement network system.

In view of their composite character, the mechanical properties of starch gels would depend, to a large extent, on their method of preparation. Conditions during gel thermosetting, as well as instrumental performance, particularly for concentrated starch dispersions, can contribute to systematic and random errors. Therefore, the variation in the measured viscoelastic parameters of replicated starch gel specimens of varying concentration, using the device of Figure 1, was first assessed. The means ($\bar{x}$), standard deviation (SD), and coefficients of variation (CV) for the storage modulus and dynamic viscosity of gels (at 1.0 Hz, 25 °C) are given in Table II. In the concentration range 8–35% (w/w), the CV for both G' and η' did not exceed 15% in all cases. The reported CV values also attest that the precision was better for gels at intermediate starch contents.

Effects of Lipids on Gelatinization and Viscoelasticity of Gels. The ability of lipids to interact with the granular starches during heating was examined by DSC. The lipids tested were an anionic (SDS) and a cationic (CTAB) surfactant, a common food emulsifier (GMS), and a zwitterionic lipid (LPC) that is one of the main internal granular lipids of cereal starches (Morrison, 1988). Typical DSC thermal curves of rice starch alone and in the presence of SDS, LPC, and CTAB are shown Figure 3; the data of transition parameters for rice and pea starches are summarized in Table III. The endothermic transition around 72–75 °C corresponds to the melting of starch crystallites, while the high-temperature endotherm is attributed to order → disorder transitions of amylose–lipid complexes (Biliaderis et al., 1986). Another low-temperature endotherm ($T_m \simeq$ 60 °C), observed only in the presence of GMS, is associated with the melting of the monoglyceride itself. Since this transition occurred in the temperature range of gelatinization of wheat, pea, and garbanzo bean starches, it made it difficult to provide true estimates of the gelatinization enthalpy of these samples (data not shown).

All additives brought about a reduction in the apparent gelatinization enthalpy of starches along with a concomitant increase of the amylose–lipid transition (Table III). The decrease in ΔH_g is interpreted as resulting from an exothermic effect due to complexation of lipids with starch molecules (Evans, 1986; Biliaderis et al., 1986); i.e., melting of starch crystallites (endothermic) is superimposed on complex formation. It was believed until recently that lipids interact mainly with the linear starch component. However, evidence from recent calorimetric studies (Evans, 1986; Eliasson et al., 1988; Levine and Slade, 1990) on waxy maize starch indicates that lipids can also complex with amylopectin. Although the nature of such complexes remains obscure, it is likely that only the longer accessible linear chains of the amylopectin molecule interact with lipids. These chains are still too short to form stable complexes that would give rise to transitions on the temperature region of the amylose–lipid complexes. Levine and Slade (1990) have recently reported a $T_m \simeq$ 70 °C for an amylopectin–sodium stearoyl lactylate complex that falls in the same temperature range as the gelatinization of most starches. Theoretically, the portion of the exothermic effect associated with the formation of amylose–lipid complexes during heating must equal their melting enthalpy. For rice starch, the data of Table III clearly show that part of the reduction in ΔH_g cannot be accounted for by formation of amylose–lipid complexes (involving both endogenous and added lipids). It is probable that the difference is due to amylopectin complexation. In contrast to native rice starch, the situation was not as clear for the defatted rice and legume starches. These samples, however, seemed to have partially lost their granular order during isolation, as evidenced by the low ΔH_g values of these materials (Table I). It is unlikely, therefore, that the thermal responses of such starch preparations can be treated by using the above rationale on the relative magnitude of opposing thermal events (gelatinization vs complexation). Among the lipids used, there were no consistent trends as far as their relative ability to complex with amylose. Nevertheless, all lipids effectively complexed with the cereal and legume starches, as evidenced by the increased ΔH_c values. In terms of transition temperatures, only SDS reduced T_{m_1} (Table III), confirming an earlier report by Gough et al. (1985). This detergent facilitates disruption of the granular organization of starches upon heating.

The storage modulus, tan δ, and dynamic viscosity values of starch gels (20 and 35% w/w) with and without added

Table II. Variation in Observed Values of Storage Modulus (G') and Dynamic Viscosity (η') of Starch Gels (1.0 Hz, 25 °C)[a]

	starch concn, %	storage modulus (G′), kPa			dynamic viscosity (η'), Pa·s		
		$\bar{x}$	SD	CV, %	$\bar{x}$	SD	CV, %
rice	8	0.2	0.1	11.2	2.2	0.1	4.5
	20	1.0	0.1	5.3	15.1	0.6	3.8
	35	5.4	0.5	9.4	144.2	21.3	14.8
garbanzo bean	8	2.4	0.3	12.8	2.3	0.1	4.3
	20	13.7	0.8	6.1	55.7	0.9	1.6
	35	58.8	5.4	9.2	276.3	58.7	6.9

[a] Number of replicate analyses ≥ 6.

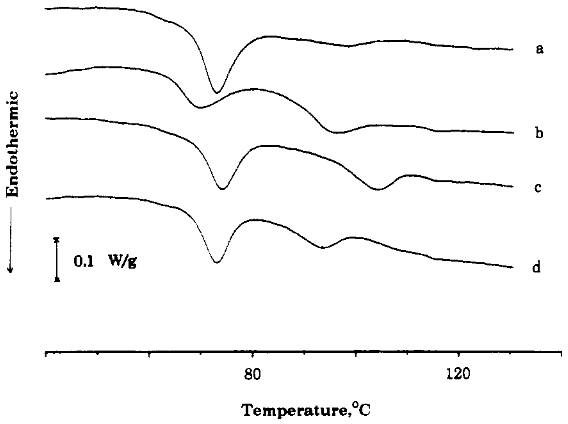

Figure 3. DSC thermal curves of rice starch alone (a) and in the presence of SDS (b), LPC (c), and CTAB (d): water content 65% (w/w), additives at 4% (w/w) on a starch basis, heating rate 10 °C/min. Weight of starch from top to bottom: 3.80, 3.79, 3.86, and 3.83 mg.

lipids are summarized in Tables IV–VI. The tan δ values were generally less than 0.1, pointing to well-cross-linked networks. There was a variation in the rheological responses of starch gels depending on the type of ligand and starch. The inclusion of lipids increased the G' and decreased the tan δ of native and defatted rice and wheat starch gels; much smaller changes were seen for pea and garbanzo bean starches. Of the additives investigated, LPC had the greatest effect on G' and tan δ, while the same ligand was the least effective in altering η'. Similar trends in the action of lipids were shown for both 20 and 35% rice and wheat starch gels. In contrast, the pea and garbanzo bean starches did not exhibit similar rheological responses (Tables IV and V); no consistent trends were shown between the pure and the lipid-fortified gels. At a given starch concentration, the G' and η' of the legume starch gels were greater than those of their cereal counterparts, presumarly due to the higher amylose content of the former.

Comparisons of the G' and η' data between native and defatted rice and wheat starches clearly indicate that removal of internal granular lipids resulted in increased gel firmness and viscosity. The improvement of gel structure after defatting is also evident from the lower tan δ values attained; tan δ is especially sensitive to changes in G' and G'' with respect to each other. A likely explanation for the above rheological responses is that granular lipids inhibit extensive exudation of amylose from the granules and thereby reduce the extent of interchain associations between linear starch molecules; noncovalent intermolecular cross-linking of amylose is pivotal to the development of a three-dimensional network. These findings concur with the higher setback viscosities reported by Melvin (1979) for defatted corn and wheat starches but do not agree with the data of Takahashi and Seib (1988), who found reduced amylogram consistencies and setbacks for low-lipid cereal starches. It should be emphasized, however, that due to the lower starch concentrations (6.5–7.5%) and shear effects in the viscoamylograph a direct comparison of these data with our findings is not appropriate.

In the context of current views on the composite nature of starch gels, explanations for their mechanical properties are often sought by considering the continuous phase (amylose network) and the embedded particles (gelatinized granules). Since the starch concentrations used in the present study (20–35% w/w) were far above the critical concentration for gelation (≈6% for most starches; Ring, 1985), it is likely that only limited swelling and amylose leaching occur, compared to that in dilute starch dispersions. With respect to the observed increases in G' of concentrated rice and wheat starch gels in the presence of lipids, a precise interpretation is not yet possible from the data of this study. It is probable that lipids complex with amylose on the granular surface and thereby restrict granule swelling; this in itself would increase the gel rigidity. Another factor that may contribute to gel strengthening is the establishment of large assemblies of helical amylose chains (V structures) in the intergranular spaces. Such ordered aggregate structures can act as physical cross-links. Finally, amylopectin complexation within the granular structures could also increase their rigidity. On the other hand, starch–lipid interactions did not appear to affect the mechanical properties of pea and garbanzo bean starch gels to any great extent (Tables IV and V). It would appear, in this case, that the linear starch fraction, present in greater amounts in these starches, dominates the network properties. Although complexation does occur upon gelatinization (Table III), the formation of a fairly rigid amylose network could mask any rigidity strengthening effects caused by the lipid. Whether the fine structure and molecular size of the starch components as well as the larger granule size of legume starches (Table I) are also influential to their gel rigidity still remains an open question. The theories on particulate-filled composite materials indicate that as particle size increases there is a decrease in the modulus due to inefficient particle packing and reduced number of interparticle contacts (Nielsen, 1974). In the case of composite starch gels, however, the amount of exuded amylose in the intergranular spaces will also increase with less densely packed granules; this would provide a better adhesion between granules and thereby increase the modulus. It is perhaps a combination of these factors that determines the net modulus value of the composite network. Clearly, more studies on carefully fractionated starch granules of different sizes, but of comparable amylose contents, are required to fully elucidate these effects.

Concentration Dependence of Storage Modulus. The variation of G' as a function of polymer concentration is often examined for physically cross-linked biopolymer gels. Clark and Ross-Murphy (1987) discussed the relationships between shear modulus (in practice, the storage modulus component, G') and concentration for protein

Table III. Melting Characteristics of 35% Starches in the Presence of Lipid Additives[a]

		starch gelatinization		amylose–lipid complex	
	additive[b]	T_{m_1}, °C	ΔH_g J g^{-1}	T_{m_2}, °C	ΔH_c, J g^{-1}
rice	control	73.2 ± 0.2^{c}	13.8 ± 0.1^{e}	98.6 ± 0.5^{b}	1.4 ± 0.1^{a}
	SDS	69.7 ± 0.1^{a}	6.7 ± 0.1^{b}	94.7 ± 1.1^{a}	6.1 ± 0.1^{d}
	CTAB	73.2 ± 0.1^{c}	7.9 ± 0.1^{c}	94.2 ± 1.1^{a}	2.9 ± 0.1^{b}
	LPC	74.2 ± 0.1^{d}	8.5 ± 0.1^{d}	104.7 ± 1.2^{c}	4.4 ± 0.1^{c}
	GMS	72.2 ± 0.1^{b}	4.0 ± 0.1^{a}	100.2 ± 0.8^{b}	2.8 ± 0.2^{b}
defatted rice	control	71.6 ± 0.2^{b}	11.1 ± 0.4^{d}		
	SDS	67.7 ± 0.1^{a}	6.0 ± 0.2^{a}	94.7 ± 0.1^{a}	3.2 ± 0.2^{b}
	CTAB	72.6 ± 0.2^{c}	8.4 ± 0.2^{c}	95.2 ± 0.4^{a}	3.1 ± 0.1^{b}
	LPC	73.4 ± 0.1^{d}	7.0 ± 0.4^{b}	105.5 ± 0.9^{c}	4.4 ± 0.1^{c}
	GMS	71.5 ± 0.4^{b}	8.3 ± 0.4^{c}	98.7 ± 0.7^{b}	2.5 ± 0.2^{a}
pea	control	59.2 ± 0.3^{b}	4.3 ± 0.3^{d}		
	SDS	54.8 ± 0.2^{a}	1.0 ± 0.1^{a}	89.0 ± 0.1^{a}	7.3 ± 0.1^{c}
	CTAB	61.3 ± 1.2^{c}	3.7 ± 0.1^{c}	90.5 ± 0.7^{b}	3.0 ± 0.3^{a}
	LPC	58.2 ± 0.1^{b}	2.8 ± 0.1^{b}	106.2 ± 0.5^{c}	4.8 ± 0.1^{b}

[a] Means ± SD ($n = 3$); values within each group followed by the same letter are not significantly different ($p \leq 0.05$). [b] Additive incorporated at a 4% (w/w) starch basis.

Table IV. Storage Modulus (G', kPa) and tan δ of 20% w/w Starch Gel at 1.0 Hz (1.8% Strain, 25 °C) in the Presence of Lipid Additives[a]

			additive[b]			
	parameter	control	CTAB	SDS	LPC	GMS
rice	G'	1.0 ± 0.1^{a1}	3.3 ± 0.2^{c2}	2.8 ± 0.1^{b1}	8.4 ± 0.6^{d2}	2.3 ± 0.2^{b2}
	tan δ	0.094	0.036	0.039	0.017	0.047
defatted rice	G'	2.1 ± 0.1^{a2}	2.7 ± 0.2^{b1}	3.2 ± 0.2^{c1}	6.7 ± 0.3^{d1}	2.9 ± 0.3^{bc2}
	tan δ	0.051	0.028	0.044	0.017	0.051
wheat	G'	1.6 ± 0.2^{b12}	3.7 ± 0.1^{d23}	3.1 ± 0.3^{c1}	6.6 ± 0.4^{e1}	1.2 ± 0.1^{a1}
	tan δ	0.127	0.081	0.072	0.029	0.116
defatted wheat	G'	3.1 ± 0.2^{a3}	4.1 ± 0.3^{b3}	5.9 ± 0.4^{c2}	11.3 ± 0.5^{d3}	4.0 ± 0.4^{b3}
	tan δ	0.098	0.080	0.080	0.018	0.071
garbanzo bean	G'	13.7 ± 0.8^{bc4}	10.0 ± 0.9^{a4}	13.4 ± 1.0^{b3}	12.8 ± 1.2^{b4}	15.1 ± 0.6^{c5}
	tan δ	0.026	0.039	0.028	0.020	0.014
pea	G'	14.3 ± 0.8^{c4}	9.6 ± 0.3^{a4}	12.5 ± 1.6^{b3}	14.8 ± 0.5^{c5}	11.9 ± 1.0^{b4}
	tan δ	0.042	0.051	0.046	0.027	0.030

[a] Means ± SD ($n = 4$); values within each group followed by the same letter (in row; additive effect) or numeral (in column; starch samples) are not significantly different ($p \leq 0.05$). [b] Additive incorporated at a 2% (w/w) starch basis.

Table V. Storage Modulus (G', kPa) and tan δ of 35% w/w Starch Gel at 1.0 Hz (1.6% Strain, 25 °C) in the Presence of Lipid Additives[a]

			additive[b]			
	parameter	control	CTAB	SDS	LPC	GMS
rice	G'	5.4 ± 0.5^{a1}	15.2 ± 0.4^{c1}	16.4 ± 0.7^{d12}	51.2 ± 1.2^{e4}	12.0 ± 0.7^{b1}
	tan δ	0.168	0.060	0.067	0.011	0.089
defatted rice	G'	7.4 ± 0.4^{a1}	14.1 ± 0.5^{b1}	14.2 ± 0.2^{b1}	36.8 ± 0.8^{d1}	18.6 ± 0.4^{c2}
	tan δ	0.114	0.078	0.077	0.022	0.070
wheat	G'	5.6 ± 0.2^{a1}	19.2 ± 1.5^{d2}	15.1 ± 1.3^{c1}	39.6 ± 1.0^{e2}	10.2 ± 1.0^{b1}
	tan δ	0.180	0.095	0.102	0.034	0.105
defatted wheat	G'	8.1 ± 0.4^{a1}	25.9 ± 2.1^{c3}	18.8 ± 0.8^{b2}	38.4 ± 2.1^{d12}	25.0 ± 0.2^{c3}
	tan δ	0.146	0.082	0.098	0.025	0.070
garbanzo bean	G'	58.8 ± 5.4^{c2}	37.5 ± 4.0^{a4}	46.5 ± 4.3^{b3}	45.6 ± 2.5^{b3}	53.7 ± 3.0^{c4}
	tan δ	0.032	0.053	0.025	0.024	0.009
pea	G'	62.2 ± 2.9^{a2}	72.8 ± 2.5^{b5}	79.8 ± 2.4^{c4}	62.4 ± 2.2^{a5}	61.2 ± 3.0^{a5}
	tan δ	0.046	0.051	0.057	0.027	0.032

[a] Means ± SD ($n = 4$); values within each group followed by the same letter (in row; additive effect) or numeral (in column; starch samples) are not significantly different ($p \leq 0.05$). [b] Additive incorporated at a 2% (w/w) starch basis.

and polysaccharide gels. They have also provided a theoretical analysis for the power law dependence of G' on polymer concentration according to which a limiting C^2 relationship is predicted at high C/C_0 ratios; C_0 is the critical concentration below which no macroscopic gel is formed. In reviewing the rheological data of various gelling biopolymers, these authors pointed out that much higher power law dependence is usually found at concentrations corresponding to C/C_0 less than 10. With respect to starch, the effect of concentration in the range 6–30% for corn, potato, and pea starch gels has been examined by using a Ward and Saunder's U-tube apparatus (Ring, 1985); for all starches linear relationships were found between the rigidity modulus and starch concentration. For corn starch

Table VI. Dynamic Viscosity ($\eta' \times 10^{-1}$ Pa·s) of Starch Gels at 1.0 Hz (25 °C) in the Presence of Lipid Additives[a]

			additive[b]			
starch concn, %	starch source	control	CTAB	SDS	LPC	GMS
20	rice	1.5 ± 0.1^{a1}	1.9 ± 0.2^{b2}	1.7 ± 0.1^{ab1}	2.3 ± 0.1^{c2}	1.7 ± 0.2^{ab1}
	defatted rice	1.7 ± 0.1^{b1}	1.2 ± 0.1^{a1}	2.2 ± 0.2^{c1}	1.7 ± 0.2^{b1}	2.3 ± 0.1^{c1}
	wheat	3.2 ± 0.6^{bc2}	4.1 ± 0.7^{c3}	3.5 ± 0.9^{bc2}	3.0 ± 0.4^{b3}	2.1 ± 0.1^{a1}
	defatted wheat	4.9 ± 0.5^{b3}	5.3 ± 0.7^{b4}	7.6 ± 0.9^{c4}	3.4 ± 0.2^{a3}	4.6 ± 0.4^{b2}
	garbanzo bean	5.6 ± 0.1^{c4}	6.1 ± 0.4^{d5}	6.0 ± 0.3^{d3}	4.4 ± 0.1^{b4}	3.6 ± 0.2^{a2}
	pea	9.6 ± 0.6^{b5}	7.6 ± 0.2^{a6}	9.1 ± 1.1^{b5}	6.6 ± 0.3^{a5}	7.2 ± 1.5^{a3}
35	rice	13.2 ± 3.0^{a1}	14.6 ± 0.7^{a1}	17.4 ± 0.8^{b1}	13.7 ± 1.6^{a12}	17.0 ± 1.1^{b2}
	defatted rice	13.5 ± 1.0^{a1}	17.6 ± 0.1^{b2}	18.0 ± 0.4^{b1}	12.8 ± 0.1^{a1}	20.8 ± 0.8^{c3}
	wheat	15.8 ± 1.1^{a1}	29.0 ± 1.4^{d3}	24.6 ± 2.3^{c2}	22.2 ± 0.7^{b4}	16.4 ± 0.4^{a2}
	defatted wheat	18.8 ± 1.5^{b2}	33.8 ± 2.8^{d4}	29.6 ± 1.6^{c2}	14.9 ± 0.9^{a2}	27.9 ± 0.6^{c4}
	garbanzo bean	27.6 ± 1.9^{c3}	36.1 ± 1.0^{d4}	37.9 ± 3.2^{d4}	17.6 ± 1.4^{b3}	10.9 ± 2.3^{a1}
	pea	45.6 ± 3.2^{c4}	60.4 ± 4.0^{d5}	72.2 ± 2.2^{e5}	25.1 ± 1.7^{a5}	28.7 ± 0.8^{b4}

[a] Means ± SD ($n = 4$); values within each group followed by the same letter (in row; additive effect) or numeral (in column; starch samples) are not significantly different ($p \leq 0.05$). [b] Additives incorporated at a 2% (w/w) starch basis.

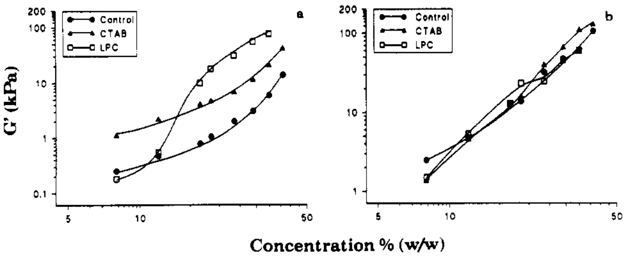

Figure 4. Experimental G' values (at 1.0 Hz and 25 °C) vs concentration of starch gels with and without added lipids (additives at 4% w/w on a starch basis): rice (a) and garbanzo bean (b).

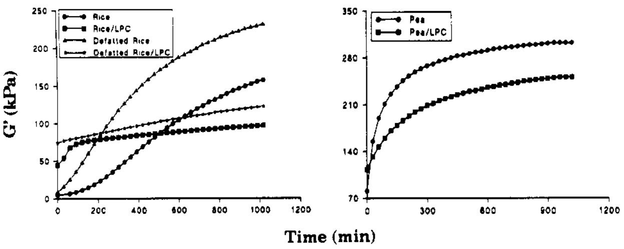

Figure 5. Storage modulus (G') vs time (at 0.2 Hz and 8 °C) for rice, defatted rice, and pea starch gels (35% w/w) alone and in the presence of LPC added at 4% (w/w) on a dry starch basis.

pastes (4–8% w/w), a linear relationship between the storage modulus (G') and concentration was also shown by small amplitude oscillatory shear testing (Evans and Haisman, 1979). In contrast, a slightly stronger concentration dependence ($C^{1.4}$) was reported by Wong and Lelievre (1981) for wheat starch pastes (2–4%) using an oscillatory coaxial cylinder viscometer. In addition to differences in sensitivity among the measuring systems used by the various researchers, the relatively low exponent values reported in these studies might be a consequence of the method of gel preparation as well as the inadequate C/C_0 range within which measurements were carried out.

In the present study, the concentration dependence of G' was examined for both rice and garbanzo bean starches alone and with added lipids over a broad concentration range (8–40%), i.e., greater C/C_0 values than in the previous studies. When the data were plotted on a log–log scale, reasonably linear plots ($r > 0.94$, $p < 0.01$) in all cases were obtained except for the LPC–rice starch gels, which gave a sigmoidal relationship (Figure 4). In accord with the single measurements at 20 and 35% solids (Tables IV and V), increases in G' of rice starch gels were observed when lipids were included over the entire range of starch concentrations (Figure 4a). In contrast, addition of lipids did not seem to affect the viscoelastic properties of garbanzo bean starch gels (Figure 4b). From the slopes ofthe linear regression lines, it was found that G' varied with concentration at $C^{2.1-2.9}$. These exponent values are indeed closer to that of the theoretical relationship $G' \alpha C^{2.0}$ than previously reported exponent values (Ring, 1985; Evans and Haisman, 1979; Wong and Lelievre, 1981). Nevertheless, it is not clear at present whether composite systems such as starch gels can be rationalized in terms of a $C^{2.0}$ concentration dependence of G'. Their viscoelastic behavior would certainly differ from that of amylose and amylopectin gels; i.e., the magnitude of the dynamic moduli of starch gels would depend not only on the density of cross-links in the continuous phase but also on the rigidity, spatial distribution, and effective contacts between the granules.

Table VII. Apparent Rate Constants (k) for Storage Modulus (G') Development (at 8 °C) of 35% w/w Starch Gels Probed by Oscillatory Shear Stress Measurements at 0.2 Hz (1.6% Strain)

	additive[a]	10^3k,[b] min^{-1}	storage modulus at 16 h (G'_c), 10^4 Pa
rice	control	4.0 ± 0.2^c ($r = 0.93$)	16.2 ± 0.6
	LPC	3.4 ± 0.2 ($r = 0.93$)	9.5 ± 0.1
defatted rice	control	4.4 ± 0.4 ($r = 0.96$)	21.8 ± 1.5
	LPC	3.4 ± 0.1 ($r = 0.94$)	11.8 ± 0.6
wheat	control	3.0 ± 0.2 ($r = 0.92$)	3.0 ± 0.1
	LPC	2.7 ± 0.1 ($r = 0.97$)	10.4 ± 0.1
defatted wheat	control	3.2 ± 0.1 ($r = 0.93$)	3.8 ± 0.1
	LPC	3.3 ± 0.1 ($r = 0.93$)	9.6 ± 0.1
garbanzo bean	control	4.3 ± 0.1 ($r = 0.97$)	30.3 ± 2.1
	LPC	3.9 ± 0.2 ($r = 0.96$)	25.2 ± 1.9
pea	control	4.7 ± 0.1 ($r = 0.98$)	30.9 ± 1.0
	LPC	4.1 ± 0.2 ($r = 0.97$)	25.8 ± 0.9

[a] Additives incorporated at a 4% w/w starch basis. [b] Determined by storage modulus measurements over time (minutes) and applying the equation $kt = \log(G'_c = G'_0/G'_c - G'_t)$: G'_0, G'_t, and G'_c correspond to time zero, t, and the completion of the experiment (16 h), respectively, while k is the rate constant. [c] Means ± SD ($n = 2$); all r values for the kinetic plots were significant ($p \leq 0.01$).

Kinetic Aspects of Starch Gelation–Retrogradation. The aggregation and gelation processes of starch and its polymeric constituents have been the subject of several recent investigations (Miles et al., 1985a,b; Ring et al., 1987; Clark et al., 1989; Biliaderis and Zawistowski, 1990). For gelation of amylose ($C > 1.0\%$), it has been suggested that rapid formation of a cross-linked network arises from the adoption of ordered double-helical chain segments, acting as "junction zones", which are interconnected by more mobile amorphous single-chain segments (Gidley, 1989). Further chain aggregation leads to crystallites capable of X-ray diffraction (B-type crystals). On the other hand, amylopectin gelation (at $C > 10\%$) is a slow process involving intra- and intermolecular chain associations. Depending on concentration, the development of shear modulus for amylopectin gels can lag behind the development of crystallites detectable by both DSC and X-ray diffraction (Ring et al., 1987). All the above time-dependent changes in the structure and properties of starch gels are collectively described by the term retrogradation.

Dynamic rheological testing is particularly useful in monitoring the kinetics of network development, provided that measurements are within the linear viscoelastic regime. Figure 5 shows the evolution of G' with time for 35% (w/w) starch gels upon storage at 8 °C. In general, the G'–time profiles revealed a biphasic gelation process: an initial rapid rise in modulus was followed by a phase of slower G' development. On the basis of our previous studies on wheat starch gelation (Biliaderis and Zawistowski, 1990), it is most likely that the former phase corresponds to amylose gelation, while the latter reflects the crystallization of amylopectin. To evaluate the effects of lipids on the mechanical properties of starch gels upon storage, the modulus data were fitted to a first-order kinetic model. Starch crystallization data are often analyzed by means of the Avrami equation, $(G'_e - G'_t)/(G'_e - G'_0) = \exp(-kt^n)$, which relates the fraction of total rheological response still to occur to time t (Wong and Lelievre, 1982); k is the rate constant, and n is the Avrami exponent. Since no apparent plateau (equilibrium, G'_e) modulus values were attained for most of the rheological experiments in the present study, it was decided to use a first-order reaction model as an empirical means of comparing gelation kinetics. It is of interest here to note that even the Avrami treatment is at best an empirical approach to describe the kinetics of starch gelation; its development is based on crystallization of pure polymers (without diluent/solvent present) and on the assumption of a single macromolecular species present. In the studies of the effect of lipids on gelation kinetics, only LPC was used. The estimated rate constant (k) values, summarized in Table VII, indicate that LPC retarded the firming process of all starch gels, particularly with respect to the slow developing modulus component (amylopectin recrystallization). These observations were further corroborated by DSC analysis of the gels over longer term storage (up to 96 h). Retrogradation of amylopectin is accompanied by the development of the "staling" endotherm (45–60 °C, Figure 6); ordering of the outer short $\overline{DP} \approx 15$ chains of the molecule has been implicated to the development of this transition (Ring et al., 1987). In agreement with the kinetic data on G' evolution, CTAB and LPC decreased the rate of amylopectin crystallization in both rice and pea starch gels (Table VIII). These findings are in accord with the calorimetric data of Russell (1983) and Eliasson and Ljunger (1988). The pea starch gels exhibited greater staling rates than those of rice starch, as assessed by DSC (Table VIII) and dynamic rheometry (Table VII). For rice starch gels, both CTAB and LPC were more effective in decreasing the staling endotherm than for pea starch, despite the higher amylopectin content of the former. While evidence for amylopectin–lipid complexation is indicated by the data of Table III and other calorimetric studies (Evans, 1986), the mechanism by which amylose–lipid interactions affect the rate of amylopectin crystallization remains unclear and warrants further investigation. It is also apparent from the findings of the present study that while LPC–rice starch gels exhibited decreased rates of staling, compared to starch alone, the G' data suggested firmer networks. Obviously, DSC and small deformation rheological testing examine different properties of the gel network, a fact that is often not appreciated by researchers in this field.

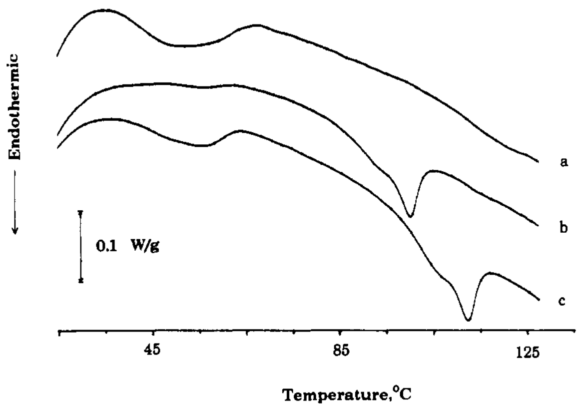

Figure 6. DSC thermal curves of defatted rice starch gels (35% w/w) after storage at 6 °C for 96 h. Lipid additives CTAB and LPC were added at 4% (w/w) on a dry starch basis, heating rate 10 °C/min. Rice starch alone (a), rice starch–CTAB, (b) and rice starch–LPC (c). Weight of starch from top to bottom: 3.82, 3.88, and 3.83 mg.

Table VIII. Starch Recrystallization in 35% w/w Gels at 6 °C[a]

starch	storage time, h	additive[b]	staling endotherm T_m, °C	staling endotherm ΔH_m, J g^{-1}
rice	4	control	57.6 ± 0.3^{b}	0.3 ± 0.1^{a}
	16		54.9 ± 0.2^{b}	2.4 ± 0.2^{b}
	48		53.6 ± 2.0^{ab}	4.2 ± 0.4^{c}
	96		50.5 ± 0.8^{a}	4.2 ± 0.5^{c}
	4	CTAB		
	16			
	48			
	96		57.0 ± 1.1	0.5 ± 0.1
	4	LPC		
	16			
	48		57.4 ± 1.1^{a}	0.5 ± 0.1^{a}
	96		56.3 ± 0.1^{a}	1.5 ± 0.2^{a}
defatted rice	4	control	56.8 ± 0.3^{a}	1.1 ± 0.1^{a}
	16		52.7 ± 2.4^{a}	2.9 ± 0.3^{b}
	48		53.7 ± 1.3^{a}	4.8 ± 0.4^{c}
	96		50.6 ± 0.3^{a}	4.9 ± 0.1^{c}
	4	CTAB		
	16			
	48			
	96		55.1 ± 0.4	0.4 ± 0.2
	4	LPC		
	16			
	48		55.4 ± 0.7^{a}	1.8 ± 0.2^{a}
	96		54.7 ± 0.1^{a}	2.3 ± 0.1^{a}
pea	4	control	59.7 ± 0.1^{b}	2.1 ± 0.2^{a}
	16		54.5 ± 0.1^{a}	3.0 ± 0.4^{ab}
	48		54.1 ± 0.1^{a}	3.5 ± 0.2^{b}
	96		54.2 ± 0.1^{a}	4.0 ± 0.2^{b}
	4	CTAB		
	16		60.4 ± 0.9^{a}	1.0 ± 0.4^{a}
	48		60.2 ± 0.1^{a}	2.3 ± 0.1^{a}
	96		57.8 ± 1.5^{a}	2.6 ± 0.4^{a}
	4	LPC	61.8 ± 0.1^{a}	0.5 ± 0.2^{a}
	16		61.1 ± 0.1^{a}	1.2 ± 0.1^{ab}
	48		59.0 ± 0.8^{a}	2.3 ± 0.4^{b}
	96		57.8 ± 0.6^{a}	2.4 ± 0.5^{b}

[a] Means ± SD ($n = 3$); values within each group followed by the same letter (column) are not significantly different ($p \leq 0.01$). [b] Additives incorporated at a 4% (w/w) starch basis.

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