

Differential Scanning Calorimetric and Rheological Study of the Gelatinization of Starch Granules Embedded in a Gel Matrix

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ABSTRACT

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The gelatinization of rice starch granules embedded in a gellan matrix or a gellan-locust bean gum matrix was investigated by differential scanning calorimetry. The same trends were found irrespective of which gel matrix was present. In the presence of the gel, the size of the endotherm per unit weight of starch appeared to decrease slightly as the concentration of the nonstarch polymer was increased, suggesting that restrictions to the extent of conformational disordering occurred. The biphasic endotherm characteristic of starch melting in concentrated starch-water mixtures was modified slightly and tended to appear more like a single peak in the presence of the gel. This may have been due to inhibition of water migration from one granule to another as the transition proceeded. The effect of gelatinization on the rheological properties of the composites

also was investigated. Small-strain oscillatory measurements demonstrated that the native starch particles reinforced the gel matrix and that this reinforcement increased if the starch was gelatinized. However, under large deformation conditions, the native granules caused the stress and strain at failure to decrease. The gelatinized particles had the same effect at relatively low concentrations. The weakening of the gel was probably caused by stress concentrations, which lead to failure, in the vicinity of the granules. At relatively high-gelatinized starch concentrations the composite was strengthened. This may have been due to an increase in the adhesion between the filler and the gel combined with the depletion of the continuous phase of the solvent.

Many cereal foods are composite materials consisting of starch granules dispersed in a gluten matrix. The granules act as filler particles in the continuous protein network (Taranto 1983). Starch can also form other composite structures. For example, starch gels are ill-defined composites consisting of swollen granules filling an interpenetrating polymer network. The major polymer in the network is amylose (Brownsey et al 1987). More clearly defined starch composites may be formed by suspending native granules in a nonstarch polymer matrix (Brownsey et al 1989). If the system is heated, the granules will gelatinize to give particles of starch gel embedded in the continuous gel phase.

The present study is concerned with a rice starch-gellan composite. The combination of rice and gellan was selected because the gelatinization temperature of the starch lies between the setting and melting temperatures of the gellan if the correct ionic environment is present (Moritaka et al 1991). This enables gels to be made that contain ungelatinized particles and allows the granules to be gelatinized without melting the gellan. A gellan-locust bean gum polymer mix also was used as the continuous phase of composites because the gel is less brittle than, but has similar melting properties to, gellan.

In the first section of the study, differential scanning calorimetry (DSC) was used to investigate the gelatinization of the rice starch in the polysaccharide matrix. Although the gelatinization of starch in pure aqueous systems is quite well understood (Biliaderis 1990), relatively little is known about the transition in complex cereal foods. The rice-gellan structure provides a model for gelatinization in such systems. Another reason for studying gelatinization in rice-gellan composites is that this may provide a means of testing Evans and Haisman's explanation of the transition (Evans and Haisman 1982). These investigators suggest that the biphasic DSC endotherms detected on heating relatively concentrated starch suspensions are associated with the migration of water. Because the continuous gel phase might be expected to limit water migration from one granule to another, the DSC endotherm could be altered accordingly.

The effect of gelatinization on the rheological properties of the composites also was investigated. Both small and large deformation tests were used. In general, the behavior of particulate biogel composites under small stress and strain regimes depends on factors such as the volume fraction occupied by the filler,

the size and shape of the particles, the rheological properties of the two phases, and the interaction between the phases (Brownsey et al 1987, Luyten and van Vliet 1990). Provided that the filler particles are rigid and at a sufficient volume fraction, reinforcement is generally obtained. There appears to be little information that describes the behavior of biocomposites under large deformations. The studies that are available indicate that strong interaction between the matrix and a rigid filler, together with a sufficient volume fraction of dispersed particles, is required to obtain reinforcement. In other cases the filler weakens the structure (Green et al 1990).

MATERIALS AND METHODS

Preparation of Composites

Rice starch was extracted as described previously (Liu et al 1991). The sample started to gelatinize at $\sim 65^\circ\text{C}$ in excess water (Liu et al 1991). To make the composites, gellan (Kelcogel, Kelco Div. of Merck & Co., San Diego, CA) or a 60:40 gellan-locust bean gum blend (Gelloid LB 100, FMC Corp., Philadelphia, PA) was dissolved in distilled deionized water by heating to 90°C . Calcium chloride (8 mM) was added, and the solution was cooled below the starch gelatinization temperature to 60°C . The required amount of rice starch (up to 50%, w/w) was incorporated, and the suspension was transferred to molds following the procedure of Brownsey et al (1987). The gels were allowed to equilibrate at 20°C for a minimum of 6 hr before use. The addition of 8 mM calcium chloride to gellan systems resulted in gel melting temperatures of $\sim 125^\circ\text{C}$.

DSC Measurements

Small cylindrical pieces of the composites were sealed in "o-ring" stainless steel pans designed to withstand high pressures and suppress the volatilization of solvent. An empty pan was used as an inert reference. The pans were heated at a rate of $10^\circ\text{C min}^{-1}$ in a Perkin-Elmer 2C calorimeter with thermal analysis data station (Perkin-Elmer, Norwalk, CT), as described previously (Liu and Lelievre 1991). All DSC traces were normalized to 1 mg of starch using the thermal analysis data station.

Small Deformation Measurements

Small deformation tests were made in the oscillatory mode using a cup-and-bob measuring system in a VOR Bohlin rheometer (Bohlin, Cranbury, NJ). Gelling solution at 90°C was poured into the cup, cooled, and held at 60°C using the rheometer temperature control. Rice starch was dispersed in the solution, and Ca^{2+} ions were added to a level of 8 mM. The bob was

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then lowered into position. The cup and contents were cooled to 25°C, and the resultant gel was then aged at this temperature for at least 1 hr. Measurements were made at 0.2 Hz and 2% amplitude while heating the composite from 25 to 90°C at 2°C min⁻¹. Linear viscoelastic behavior was observed in this strain range.

Large Deformation Measurements

A composite containing ungelatinized starch granules was prepared in the form of a cylinder (diameter, 21 mm; length, 19 mm). Samples containing gelatinized starch, obtained by heating the composites at 95°C for 30 min in a water bath, were also studied. All the specimens were compressed between lubricated, flat, Teflon surfaces fitted to an Instron universal testing machine (Instron, Canton, MA), as described previously (Lelievre et al 1992). The gels were deformed at a constant speed of 50 mm min⁻¹ to failure. Load-deformation data were recorded, and the true stress and Hencky's strain were calculated.

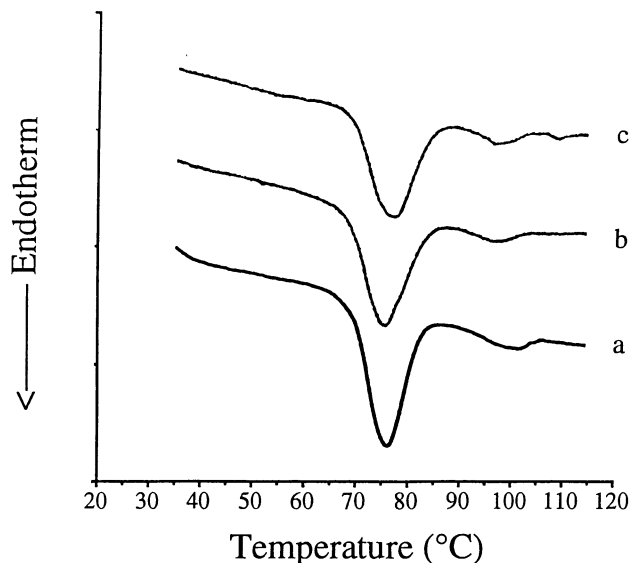


Fig. 1. Differential scanning calorimetry traces for starch (30%) heated in pure water (a), 0.8% gellan (b), and 1.5% gellan (c). Heat flow axis, 250 $\mu\text{J sec}^{-1}$ per division. All traces were normalized to 1 mg of starch.

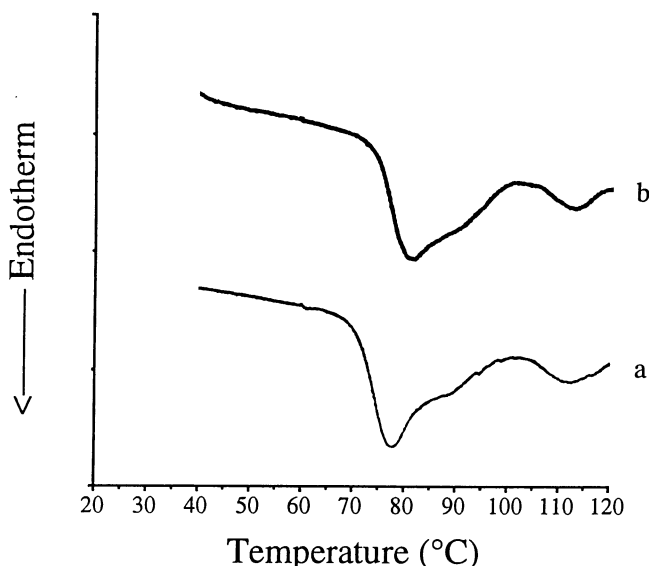


Fig. 2. Differential scanning calorimetry traces for starch (50%) heated in pure water (a) and in 1% gellan-locust bean gum gel (b). Heat flow axis, 150 $\mu\text{J sec}^{-1}$ per division. All traces were normalized to 1 mg of starch.

RESULTS AND DISCUSSION

The same trends were obtained irrespective of whether the granules were embedded in a gellan matrix or a gellan-locust bean gum matrix.

DSC Traces

Figure 1 shows DSC traces obtained upon heating starch (30%) contained in gels made of various concentrations of gellan. The size of the endotherm appears to decrease slightly as the concentration of the polymer is increased. The explanation of this effect is uncertain, but there may be restrictive effects on the extent of conformational disordering of the starch polymers in the nonstarch matrix (Wootton and Bamunuarachchi 1980). Wootton and Bamunuarachchi (1980) suggested that such changes in conformational disordering might contribute to a decrease in endotherm size by reducing the energy difference between the granular and gelatinized starch.

Figure 2 demonstrates that the presence of the gel matrix tends to slightly modify the standard biphasic endotherm, obtained with concentrated starch suspensions in pure water, to give something that approaches a single peak. If the presence of the nonstarch polymer phase inhibits water movement from granule to granule, then the results in Figure 2 are consistent with the suggestion that the biphasic behavior stems from the redistribution of water within the sample (Evans and Haisman 1979). This conclusion is reinforced by recent work on the gelatinization of rice-wheat starch blends (Liu and Lelievre 1992).

Small Deformation Properties

Figure 3 shows that when pure gellan is heated from 45 to 90°C, change in the dynamic rigidity is minimal. The figure also demonstrates that the presence of ungelatinized starch in the gel causes some reinforcement. When the starch gelatinizes, the dynamic rigidity increases markedly to a value that remains constant once the transition is complete. The corresponding dynamic viscosity remains virtually unchanged until gelatinization occurs, whereupon the value decreases to a fixed level (data not shown). This trend, which is in effect a mirror image of that exhibited by the rigidity, suggests that the gel is becoming more elastic when gelatinization takes place. On cooling the system from 90°C to room temperature, the values of the dynamic rigidity and viscosity remain about the same (data not shown). The fact that the gelatinized granules cause more reinforcement than the native starch, despite the fact that the latter particles are more rigid, could be due to a number of factors. For example, on gelatinization the volume fraction occupied by the granules increases, the gel phase is depleted of water and therefore becomes more rigid, and the adhesion between the filler and matrix may improve.

Figure 4 shows that the dynamic rigidity increases more rapidly with gelatinized starch concentration when the filler exceeds about 8%. At about this concentration the gelatinized granules start to become closely packed, suggesting that a continuous network of filler gel particles is formed within the gellan framework that could lead to the marked rigidity increase. The rheological proper-

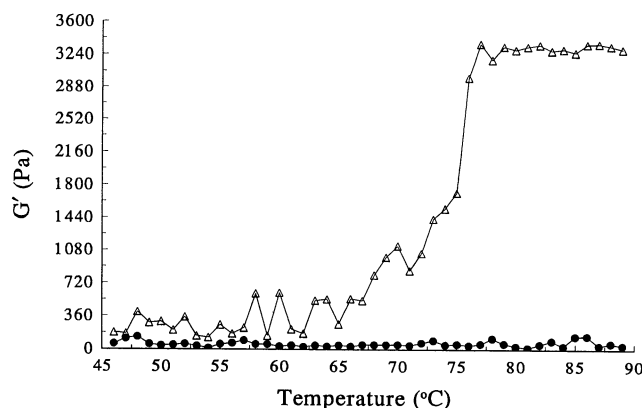


Fig. 3. Dynamic rigidity of 1% pure gellan gel (●) and of 1% gellan gel containing 10% rice starch (Δ) as a function of temperature.

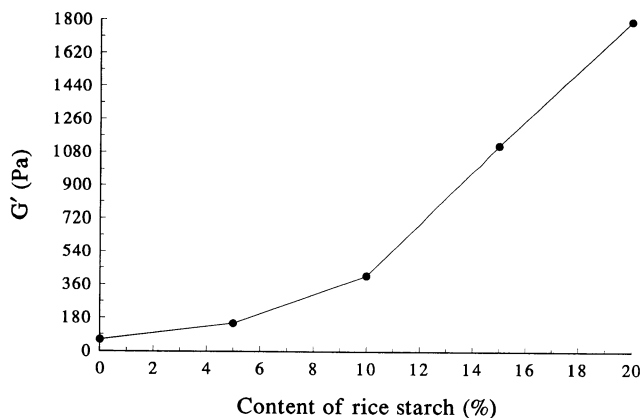


Fig. 4. Dynamic rigidity of rice starch and gellan-locust bean gum (1%) composites at 80°C as a function of starch content.

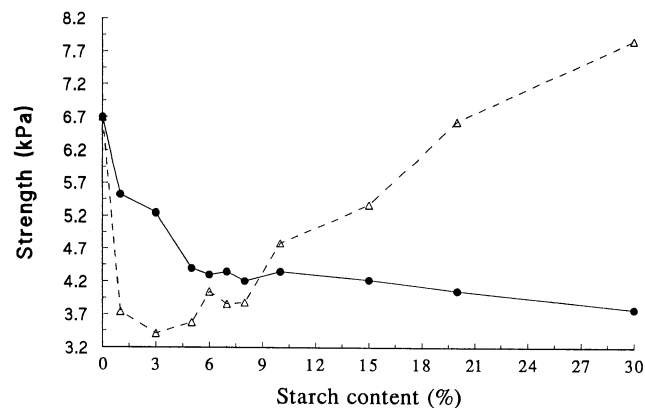


Fig. 7. Strength (failure stress) of composites (rice starch in 1% gellan gel) versus starch content. ●, Composites containing ungelatinized starch; △, composites containing gelatinized starch.

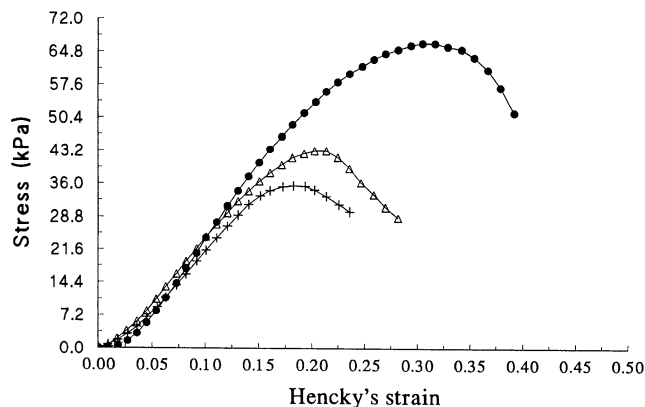


Fig. 5. Compressive failure of 1% gellan gel (●), 1% gellan gel containing 5% ungelatinized rice starch (△), and 1% gellan gel containing 5% gelatinized rice starch (+).

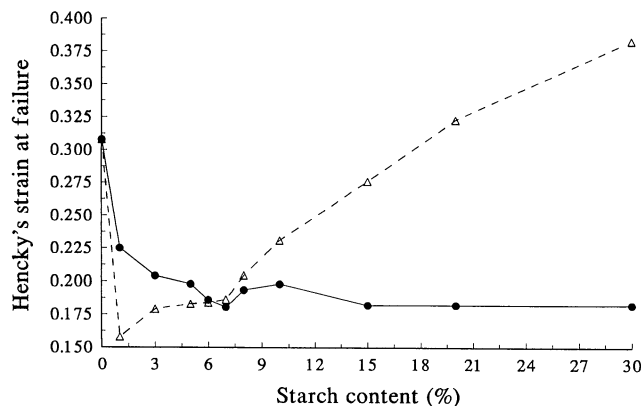


Fig. 6. Failure strain of composites (rice starch in 1% gellan gel) versus starch content. ●, Composites containing ungelatinized starch; △, composites containing gelatinized starch.

ties of starch pastes have been shown to change dramatically when such a closely packed structure exists (Evans and Haisman 1979).

Large Deformation Properties

Relatively low concentrations of granules were found to cause the stress and strain at failure of gels to decrease (Fig. 5). This type of behavior suggests that adhesion between the filler and matrix is relatively weak and that stress concentrations in the vicinity of the disperse particles lead to premature failure of the gel phase. Figures 6 and 7 show that when the concentration of ungelatinized starch is increased, the stress and strain at failure decrease further. This is consistent with the view that stress concentrations are leading to gel failure. However, when the concen-

tration of gelatinized starch is increased, reinforcement is ultimately obtained and both the stress and strain at failure increase. Comparison with other polymer composites suggests that this increase could be due to an improvement in the adhesion between the gelatinized filler and the matrix and to an increase in the volume fraction occupied by the disperse particles. The depletion of water in the gellan phase also could play a role (Brownsey et al 1987, Luyten and van Vliet 1990).

ACKNOWLEDGMENT

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