
Phase behaviour and rheology of mixed polymer systems containing starch

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Abstract. Studies have been undertaken to monitor the phase behaviour of potato maltodextrin (PMD) in admixture with locust bean gum, gum arabic and carboxymethyl cellulose. Two phase liquid separation occurred at low total polymer concentrations for PMD/locust bean gum mixtures and the threshold concentration in water was ~3.5 and 2.8 wt% in 0.1 mol/dm³ NaCl. Very much higher concentrations were required for the PMD/gum arabic system (threshold concentration in water >47 and 16 wt% in 0.1 mol/dm³ NaCl. Carboxymethyl cellulose only induced phase separation if electrolyte was added and the threshold concentration was 10.8 wt%. The rheological properties of PMD were greatly influenced by the addition of gum arabic. At low additions, the storage modulus (G') was greatly enhanced, while at higher additions, corresponding to compositions in the two phase region of the phase diagram, lower values of G' were obtained. The rate of PMD gelation followed first order kinetics and the rate constant increased with increasing gum arabic concentration.

Introduction

Modified starches are often used in the food industry to control the rheological and textural properties of food products. However, it has been found that the 'mouthfeel' of many preparations can be improved by the addition of other polysaccharides to the formulation (1). The resultant shelf life of the food product may also be improved by the addition of some hydrocolloids, which slow down the rate of retrogradation of the starch and thus reduce the degree of syneresis.

Native starch is composed of a mixture of two polymers. The minor component, amylose, is a linear molecule consisting of α -1,4-linked D-glucopyranose units whilst the higher molecular weight amylopectin also contains branches occurring through α -1,6-linkages (2). Typical concentrations of amylose to amylopectin are 20:80 although this is dependent on the botanical source (3).

Gelatinisation of native starch in excess water occurs at a temperature which is typical for the particular starch. Gelatinisation involves the irreversible swelling of starch granules, with the loss of molecular order, followed by solubilisation of amylose (4). The amylose chains can associate (retrograde) and lead to gel formation. The rheology of starch gels is thus considered to be consistent with those of 'filled gels' and as such will be determined by factors such as the shape of the amylopectin molecules, their deformability and size and hence the volume fraction occupied (5).

The starch used in this study is an α -amylase hydrolysis product of potato

starch, i.e. potato maltodextrin (PMD). It is very slightly charged due to the occurrence of residual phosphate groups present in the amylopectin molecule of the native potato starch (6). α -Amylase hydrolysis preferentially shortens the amylose chains (2). The resulting product has increased solubility and clarity and its phase behaviour in mixed polymer solutions can be readily studied (7). The characteristics of mixed PMD/hydrocolloid systems will be determined mainly by the compatibility of the amylose–hydrocolloid molecules and this will also determine the resultant rheology and texture of the gel (8,9).

The following experiments look at the phase behaviour of PMD with a number of hydrocolloids and the consequence of this on their rheological properties.

Materials and methods

PMD, labelled C☆ PUR 01906 was supplied by Cerestar. Locust bean gum (LBG) and carboxymethyl cellulose, (CMC, degree of substitution 0.7, molecular mass 90 000) were supplied by Hercules. Gum arabic (Acacia Senegal) was supplied by Agrisales UK. It was shown to contain 11% rhamnose, 23% arabinose, 41% galactose, 20% glucuronic acid and 2% protein. The specific rotation was -30° .

Sample preparation

Concentrated PMD solutions were prepared on a weight for weight basis by heating PMD in distilled water in a boiling water bath for 30 min with gentle shaking to ensure homogeneity. Minimal shear of the solution was exercised so that the integrity of the molecules was retained and reproducibility of each sample was ensured. A correction was later made for any loss due to evaporation.

Gum arabic solution (40 wt%) was prepared in distilled water by stirring overnight at room temperature followed by filtration through a wide mesh sieve to remove any debris and centrifugation at ~ 3000 g.

LBG and CMC stock solutions were prepared in distilled water with heating to 2.0 and 10 wt% respectively.

Phase behaviour

PMD and the various hydrocolloid stock solutions were equilibrated at 45°C for 10 min prior to mixing on a weight for weight basis. The samples were shaken, replaced in the water bath at 45°C (10 min) and then centrifuged at 3000 g for 10 min. Samples were then stored at 45°C and the phase behaviour noted. This temperature was chosen since PMD does not gel under these conditions over the timescale of the phase behaviour study (2–3 days) (7).

Rheological measurements

PMD/hydrocolloid mixtures were prepared by dissolving PMD in distilled water in a boiling water bath (5 min) and then adding accurately a given amount of

hydrocolloid stock solution. The resultant mixture was heated for 30 min with occasional shaking and any loss due to water evaporation accounted for.

Samples (9 cm³) were loaded hot onto a Carrimed CS100 rheometer equipped with concentric cylinder geometry and covered with a thin coat of silicone oil to prevent evaporation. Small deformation oscillatory measurements were performed as a function of time at a temperature of 25°C. A frequency of 1 Hz and a displacement amplitude of 1 milli-radian were used and the results accumulated over a period of 15 h.

Rate of gelation

The rate of gelation of the PMD/hydrocolloid systems was calculated using the following equation which assumes first order reaction kinetics (10).

$$G(t) = G_{\text{sat}} (1 - e^{-kt}) \quad (1)$$

where G_{sat} = plateau value of G' , k = rate constant of the gelation, t = time.

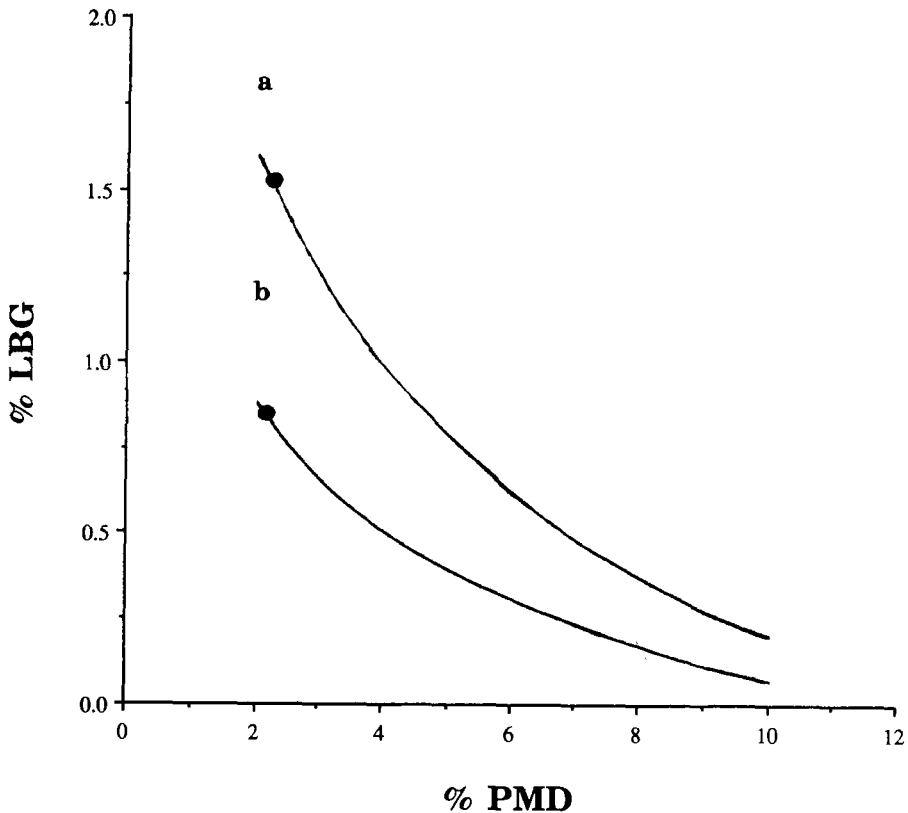


Fig. 1. Phase diagram of PMD and LBG in admixture at 45°C (a) in the absence of electrolyte (b) in 0.1 mol/dm³ NaCl. ● represents the threshold value.

Results

The phase diagrams for mixtures of PMD and LBG are shown in Figure 1. Two liquid layers were formed at higher polymer concentrations and the phase boundaries separating the single and two phase regions are depicted with (a) representing that of the PMD/LBG system in water and (b) the same system in $0.1 \text{ mol/dm}^3 \text{ NaCl}$. The addition of NaCl lowers the concentrations at which phase separation occurs. The threshold concentration, defined as the minimum total polymer concentration necessary for phase separation to occur was 3.5 wt% in water and 2.8 wt% in NaCl.

The phase diagrams for the PMD/gum arabic system are shown in Figure 2. Again phase separation occurs and the two phase boundaries represented are (a) in the absence of and (b) in the presence of $0.1 \text{ mol/dm}^3 \text{ NaCl}$. Similar results to those in Figure 1 are obtained; however the total polymer concentrations required for phase separation are greatly enhanced. The threshold concentrations are 47 and 16 wt% in water and $0.1 \text{ mol/dm}^3 \text{ NaCl}$ respectively.

Figures 3a and b represent the phase behaviour of PMD with CMC in the

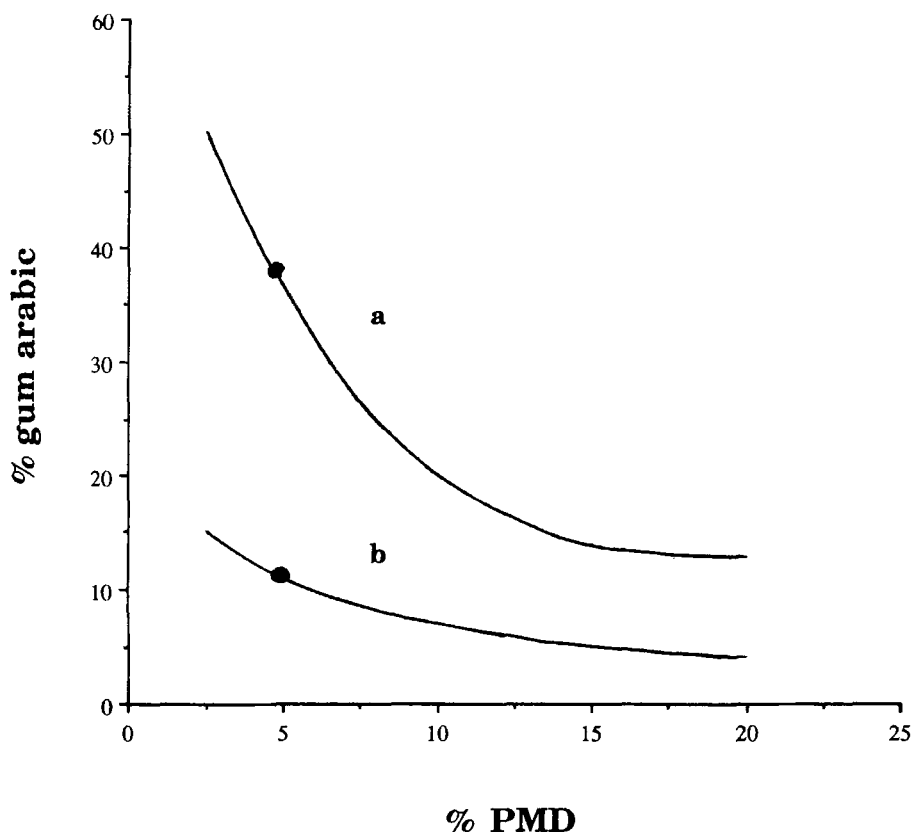


Fig. 2. Phase diagram of PMD and gum arabic in admixture at 45°C (a) in the absence of electrolyte (b) in $0.1 \text{ mol/dm}^3 \text{ NaCl}$. ● represents the threshold value.

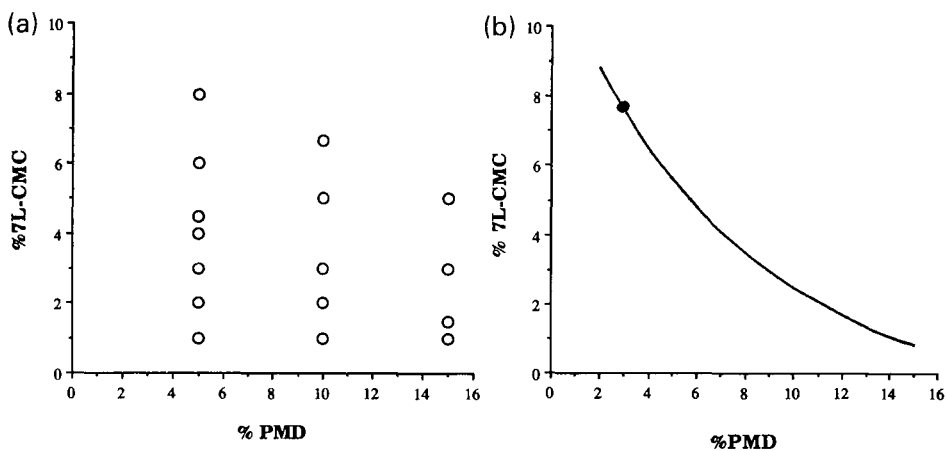


Fig. 3. (a) Phase diagram of PMD and CMC in the absence of electrolyte at 45°C. Circles represent non-phase separated concentrations of polymers. (b) Phase diagram of PMD and CMC in admixture in the presence of 0.1 mol/dm³ NaCl at 45°C. ● represents the threshold value.

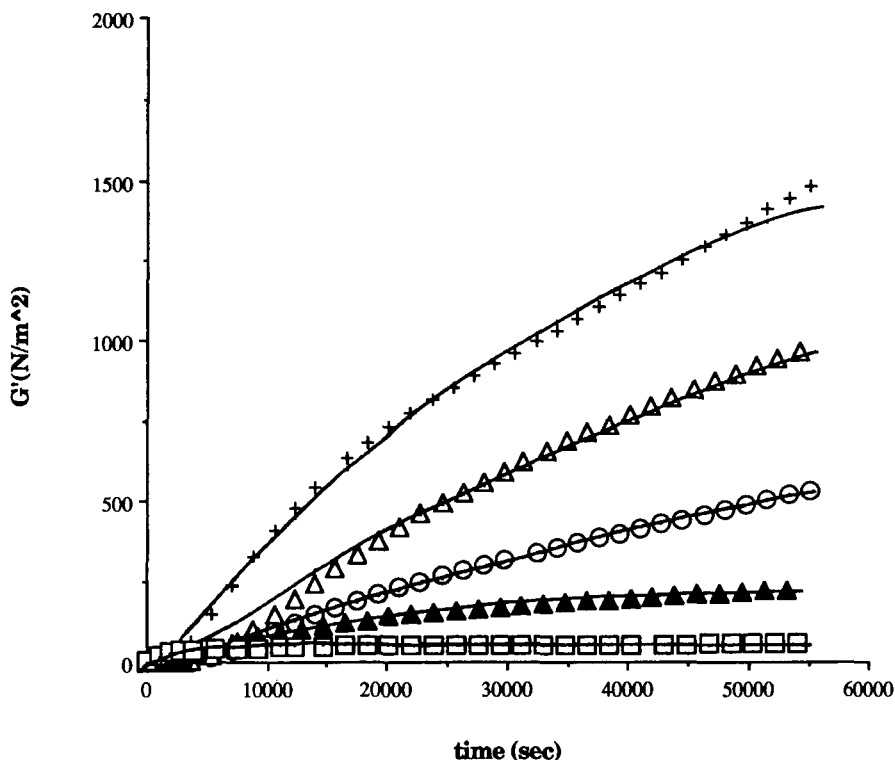


Fig. 4. Storage modulus as a function of time for mixed systems at 25°C containing a fixed concentration of PMD (10 wt%) with increasing concentrations of gum arabic. ○, +10% GA; Δ, +12% GA; +, +15% GA; ▲, +20% GA; □, +25% GA. Solid lines represent theoretical fitted values calculated using equation (1).

absence and presence of electrolyte respectively. In this case, phase separation only occurred if electrolyte was present and the threshold value was ~ 10.8 wt%.

Storage moduli, G' , for the mixed systems containing 10 and 20% PMD are depicted as a function of time for increasing concentrations of gum arabic in Figures 4 and 5 respectively. The magnitude of G' after 15 h is seen to increase initially with increasing gum arabic concentration but then decreases at gum arabic concentrations of $>15\%$. This is more clearly illustrated in Figure 6.

The solid lines in Figure 4 for the 10% PMD/gum arabic systems are the theoretical rate curves calculated using equation 1 and show a reasonably good fit. Similarly, theoretical fitted values are shown for the 20% PMD systems in Figure 5. The calculated rate constants are plotted as a function of concentration of gum arabic for systems containing 10 and 20% PMD in Figure 7.

Discussion

In ternary systems containing two polymers in a common solvent, the polymers may or may not associate. Association can lead to the formation of a precipitate

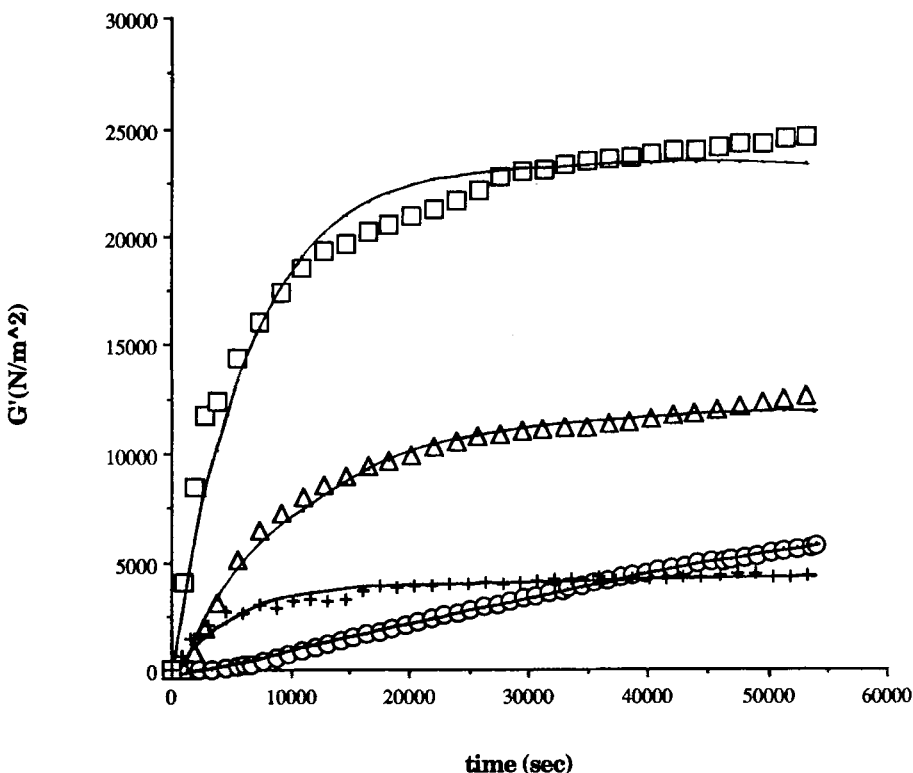


Fig. 5. Storage modulus as a function of time for mixed systems at 25°C containing a fixed concentration of PMD (20 wt%) with increasing concentrations of gum arabic. \circ , +0% GA; Δ , +5% GA; \square , +10% GA; $+$, +20% GA. Solid lines represent theoretical fitted values calculated using equation (1).

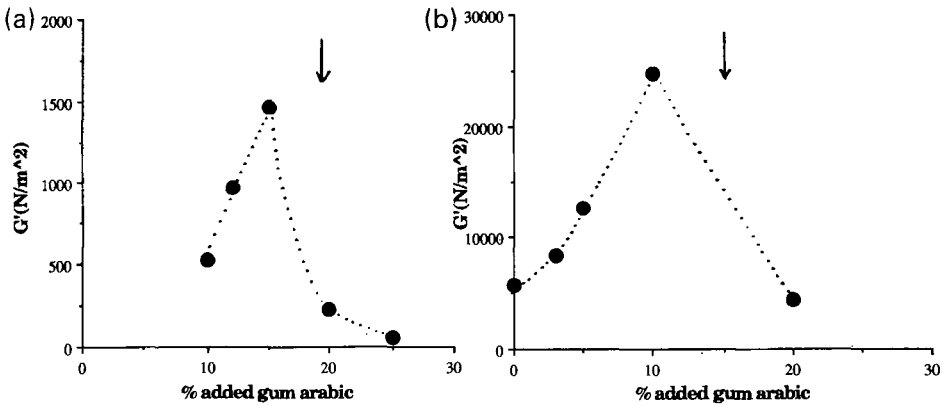


Fig. 6. (a) Storage modulus after 15 h at 25°C as a function of concentration of added gum arabic to a fixed PMD concentration (10%). The arrow represents the concentration of gum arabic at which phase separation was noted for similar mixtures held at 45°C. (b) Storage modulus after 15 h at 25°C as a function of concentration of added gum arabic to a fixed PMD concentration (20%). The arrow represents the concentration of gum arabic at which phase separation was noted for similar mixtures held at 45°C.

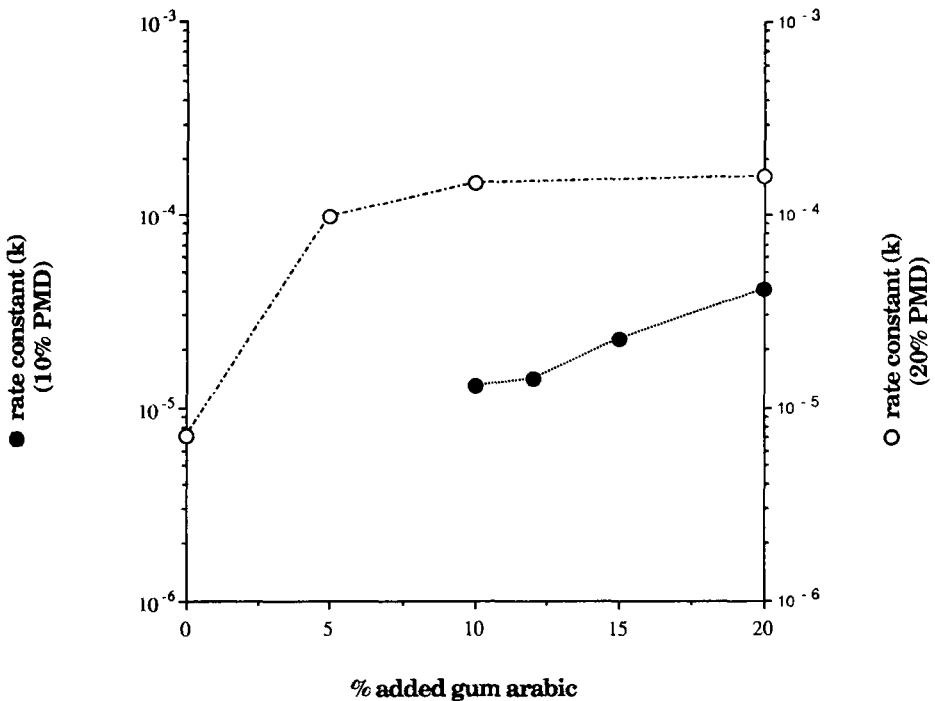


Fig. 7. (a) Rate constants as a function of added gum arabic to a fixed PMD concentration (10%). (b) Rate constants as a function of added gum arabic to a fixed PMD concentration (20%).

(coacervate) as for instance in the case of oppositely charged polymers, e.g. whey proteins and carboxymethyl cellulose (11) or to the formation of a three dimensional gel structure, e.g. xanthan and konjac mannan (12). If the polymers are non-associating then they may be present in solution as a single homogeneous phase or they may segregate and form two separate liquid phases.

For mixtures of two uncharged polymers in solution, the free energy of mixing is usually dominated by the small but positive enthalpic term. This is sufficient to compensate for the low entropy term associated with the mixing of large polymer molecules and therefore, the mixing becomes thermodynamically unfavourable and segregation of the two polymers occurs at sufficiently high polymer volume fractions. Phase behaviour can be predicted with some success using Flory–Huggins theory (13). If one of the polymers carries an ionic charge, the entropy of mixing becomes large due to the presence of the polymer counterions. Confinement of the counterions to one liquid layer of lower volume is thermodynamically unfavourable and hence segregation does not occur. The addition of electrolyte to such a system, however, reduces this effect since there can be free exchange between the counterions in the two phases and hence polymer segregation is promoted. If both polymers contain a similar proportion of charges (of the same sign) then segregation occurs as in mixtures of uncharged polymers and the phase behaviour is insensitive to the addition of electrolyte. Such effects have recently been discussed by Piculell *et al.* (14, 15) from both an experimental and theoretical viewpoint.

The systems studied in the present work reinforce these general concepts. Thus for the mixture of PMD and LBG, two essentially uncharged polymers, phase separation occurs at quite low LBG concentrations. The fact that the phase boundary shifts to lower polymer concentrations in the presence of electrolyte may be due to the fact that there are a small number of phosphate groups on the PMD chains. For the other two systems studied involving PMD in combination with a charged polymer, phase separation was more difficult to achieve. In the case of CMC, phase separation could not be observed at all in the absence of electrolyte for the compositions investigated but was observed when electrolyte was present. With gum arabic, phase separation was observed without added electrolyte but only at very high polymer concentrations. Such concentrations were inaccessible for the PMD/CMC system because the viscosity would have been too high. As expected the phase boundary for the PMD/gum arabic mixture shifted to lower concentrations on addition of electrolyte.

The increase of G' for PMD and PMD/gum arabic systems is attributed to gel network formation brought about by the association of amylose (and to a lesser extent amylopectin) chains. Gum arabic is itself non-gelling and it is unlikely that the PMD and gum arabic molecules associate to form a coupled network. In the case of 10% PMD alone, no gel formation takes place, however, the experiments have shown that a gel is formed on addition of 10% gum arabic and that the rate of gel formation increases gradually as the concentration of gum arabic increases. For the 20% PMD system (which is itself gelling), a large increase in the rate of gelation occurs on addition of gum arabic to the system. At low gum arabic concentrations where the PMD and gum arabic molecules co-

exist as a single homogeneous phase, G' increases considerably compared to PMD alone indicating a more extensively associated PMD gel structure. At higher gum arabic concentrations where polymer segregation occurs, G' for the mixture has similar values to PMD alone indicating that the enhanced rate of amylose association results in a less extensive, weaker three dimensional gel structure.

Rheological results reported for maize starch/locust bean gum systems (9) also described a maximum in the G' /time profiles as the concentration of LBG was increased. Similarly, the authors attributed the subsequent decrease in G' to incompatibility between the galactomannan and amylose in the continuous phase leading to a two phase system although this could not be directly observed.

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