Carbohydrate Polymers **19** (1992) 211–218

Dynamic rheological studies on an interaction between lipid and various native and hydroxypropyl potato starches

Hak Ryang Kim, Ann-Charlotte Eliasson & Kåre Larsson

Department of Food Technology, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden

(Received 10 April 1992; accepted 18 May 1992)

Dynamic rheological measurements and differential scanning calorimetry (DSC) were used to investigate the interaction between starches and lipid. The starches used were waxy maize starch, native potato starch, and hydroxypropyl potato starches with varying molar substitution (MS). The lipid chosen was a monoglyceride, monomyristin (MGM). A Brabender amylograph was used to prepare starch pastes with and without MGM. The rheological behaviour of the starch pastes was evaluated after the preparation, and during heating and subsequent cooling. The influence of an addition of MGM on the rheological behaviour was much higher for the native potato starch than for the waxy maize starch, and decreased as the MS of hydroxypropyl potato starches increased.

On heating, waxy maize starch–MGM paste gave one rheological transition at temperatures below about 65°C. Native potato starch and hydroxypropyl potato starch (MS 0·045)–MGM pastes showed two rheological transitions, one of which had a similar temperature range to that of the waxy maize starch–MGM paste. The other one, which was observed as a sharp decrease in the storage modulus (G') and an increase in the phase angle (δ), provided rheological evidence for the dissociation of an amylose–MGM complex, and it occurred at nearly the same temperature as the endothermic transition of the amylose–MGM complex measured by DSC. On cooling, this rheological behaviour of the starch–MGM pastes was reversed, indicating that an association between starch and MGM took place. The results of this study gave further rheological evidence for an interaction between amylopectin and MGM.

INTRODUCTION

The interaction between starch and lipids has important consequences for foods and technical applications in order to achieve the desired physicochemical properties. In food applications, lipids have been conventionally utilized to modify the rheological and textural properties of starch pastes, the effect being widely attributed to a complex formation with amylose. The behaviour of amylopectin in relation to lipids is still unclear although it is the major component of normal starches. However, there have been some indications of an interaction between amylopectin and lipids (Batres & White, 1986; Hahn & Hood, 1986; Eliasson & Ljunger, 1988).

In most previous studies, the rheological behaviour of starch in the presence of lipids has been studied with a Brabender Amylograph (Krog, 1973; Orthoefer, 1976; Riisom *et al.*, 1984; Takahashi & Seib, 1988), in which the structure of the starch is continuously changed due to the combined influences of temperature, shear and time on the starch granules. An alternative is to use dynamic rheological methods in which a small deformation is given to the material, thus keeping the structure of the material unaltered during measurements.

When lipids are added to a starch paste in real applications, it is of importance to investigate the rheological behaviour also after preparation and not only during the preparation (gelatinization of starch).

In the present study, dynamic rheological measurements were used to investigate the interaction between starch and a monoglyceride, monomyristin (MGM). The MGM was chosen because it has a high complex forming ability with amylose (Krog, 1973; Hoover & Hadziyev, 1981). Differential scanning calorimetry

Carbohydrate Polymers 0144-8617/92/$05.00

(DSC) was used to follow thermal transition properties of the starch-MGM sample. The importance of the nature of starch for starch-MGM interactions was studied for different types of starches; waxy maize starch, native potato starch and hydroxypropyl potato starch with varying molar substitution (MS).

MATERIALS AND METHODS

Materials

The starch samples used were a waxy maize starch, a native potato starch, and three hydroxypropyl potato starches with MS of 0·045, 0·125 and 0·170, respectively. The waxy maize starch and native potato starch were obtained from Stärkelsen (Kristianstad, Sweden). The native potato starch was the parent starch for the preparation of the hydroxypropyl potato starches. The preparation methods and some physicochemical properties of them are described elsewhere (Kim *et al.*, 1992).

The monomyristin (MGM) used was obtained from Grinsted Products (Brabrand, Denmark). It was an industrially distilled product, and contained 0·2% monolaurin, 4·1% monopalmitin and 0·5% monostearin, besides MGM.

Methods

DSC measurements

The thermal transitions of the gelatinized starch-MGM mixture were observed with a Perkin-Elmer DSC 2. MGM in the form of crude powder was finely ground using a mortar. The MGM (0·5 g) was mixed with 10 g of starch sample, and then shaken vigorously. About 3–4·5 mg of the mixture was transferred into a weighed sample pan, and water was added to give a mixture:water ratio (w/w) of about 1:3. After sealing the pan, it was heated at 120°C for 15 min in an oven. After cooling to room temperature, it was scanned from 22°C to 120°C at a rate of 10°C/min, with an empty pan as a reference. Each measurement was at least triplicated. The enthalpy (J/g) and the temperatures of onset (T_o), peak (T_p) and conclusion (T_c) of a peak were evaluated by the method of Eliasson (1986).

Preparation of starch samples

A Brabender Amylograph was used for the preparation of starch pastes with and without MGM using a pasting procedure described elsewhere (Eliasson & Kim, 1992). The concentration of starch (dry basis) was 5% for potato starches and 10% for waxy maize starch. When starch-MGM pastes were prepared, MGM as a crude powder was added into the heated starch at 95°C in the beginning of the cooling process.

The amount of MGM added to potato starches was 5% (w/w), based on the starch. To the waxy maize starch, 2·5% MGM was added, since this starch has a lower binding ability to lipids than normal starches (Hahn & Hood, 1986).

Rheological measurements

The measurements were performed in the oscillation mode in a Bohlin VOR Rheometer (Lund, Sweden), equipped with a programmable water bath. The C-25 measuring system was used at a frequency of 0·9 Hz and a strain of 0·0206. At this strain, all samples were well within the linear region.

During the preparation in the Brabender Amylograph, many air cells were introduced into the samples. When the samples were used to investigate the rheological behaviour during heating and subsequent cooling, they were degassed by vacuum suction, since it was believed that the presence of the air cells caused larger alteration to the rheological behaviour than the disruption of the gel structure, caused by the degassing procedure.

The degassed samples were heated from 25°C to 90°C at a rate of 1·5°C/min, and held at 90°C for about 1 min for the changing of the computer program to one for cooling, and then cooled to 25°C at a rate of 1·5°C/min. The initial equilibrium time was 60 s, and the dynamic rheological parameters were monitored every 30 s. In order to prevent evaporation of water during measurements, the starch sample was covered with a thin layer of silicon oil (low viscosity).

All rheological measurements began within 10 min after sample preparation in the Brabender Amylograph.

RESULTS AND DISCUSSION

DSC properties

The thermograms of the mixtures of the gelatinized starch-MGM are shown in Fig. 1. The excess MGM, which had not reacted with the gelatinized starch, gave an endothermic transition below 40°C. Thus, the

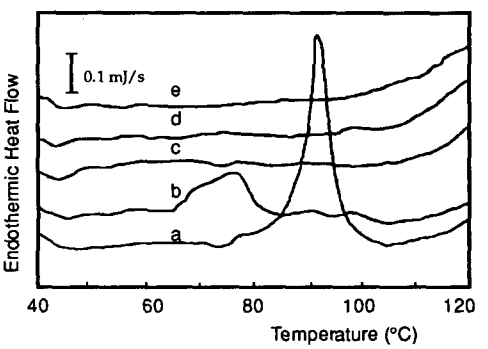

Fig. 1. DSC thermograms of the mixtures of monomyristin and (a) gelatinized native potato starch; hydroxypropyl potato starches with (b) MS 0·045; (c) MS 0·125; (d) MS 0·170; (e) waxy maize starch.

40–120°C temperature range of the thermogram is presented.

The mixture of a gelatinized native potato starch and MGM showed an endotherm, with T_o, T_p and T_c being 78·5 ± 0·6°C, 92·5 ± 0·7°C and 103·4 ± 0·6°C, respectively. The enthalpy was 6·4 ± 0·4 J/g. When the native potato starch was hydroxypropylated to MS 0·045, the endotherm became broader, and the temperatures were lowered, i.e. T_o = 66·3 ± 0·3°C, T_p = 77·3 ± 0·4°C and T_c = 81·3 ± 0·2°C. The enthalpy was reduced to 1·6 ± 0·3 J/g.

It is interesting to see that the hydroxypropylation of native potato starch to MS 0·045 lowered the endothermic temperatures by about 15°C, and reduced the enthalpy by about 75%, compared with the corresponding values obtained for the mixture of a gelatinized native potato starch–MGM. No endotherms were detected in the starch–MGM mixtures of the gelatinized hydroxypropyl potato starches with MS 0·125 and 0·170, or waxy maize starch.

Rheological properties

Comparison of the rheological properties at 25°C of starch pastes, with and without MGM

The rheological properties of starch pastes, with and without (control) MGM, are shown in Table 1. These rheological values were obtained at 25°C after the preparation of the samples from a Brabender Amylograph, without degassing. The rheological values, G' (storage modulus), G'' (loss modulus) and (δ) (phase angle) of the control potato starch pastes differed slightly, depending on the MS. This would be due to the different susceptibility of the starch granules to heat and shear during cooking.

An addition of MGM into the control starch pastes caused marked changes in the rheological properties. In general, the starch–MGM pastes had more elastic structures with increased G' and decreased δ values. The added MGM had a large influence on G', while G'' remained almost unaltered. The extent of the changes was very dependent on the MS. The addition of MGM to waxy maize starch resulted in an increase in G' of 33·2 Pa and a decrease in δ of 17·0, compared to the control.

It might be expected that all MGM added did not react with starch, and the unreacted MGM could influence the rheological values in Table 1. When a native potato starch (5%) is cooked with addition of 5% lecithin (based on the starch) under the same pasting conditions used in this study, the G', G'' and δ of the potato starch–lecithin paste were 21·1 Pa, 10·4 Pa and 25·2°, respectively (Kim, 1992). These values are near to those of the control of native potato starch in Table 1. Eliasson (1986) detected no interaction between lecithin and potato starch by DSC measurement.

It is tempting to suggest that the variation in rheological values with and without MGM, shown in Table 1, reflects the differences in the ability of different types of starches to react or bind with MGM. The result indicated that waxy maize starch reacted with MGM. The interaction between potato starches and MGM decreased as the MS increased, possibly due to the hydroxypropyl groups on the starch molecules, which sterically hinder the complex formation. Our results agree with the report on the binding ability of a waxy maize, a native corn starch and a hydroxypropyl corn starch to stearic acid, as investigated by equilibrium dialysis technique (Hahn & Hood, 1986).

Rheological behaviour during heating and cooling of starch pastes with and without MGM

Waxy maize starch. A waxy maize starch, known to be nearly free of amylose, was used in order to investigate if there is an interaction between amylopectin and MGM. Figure 2 shows the rheological behaviour during heating and subsequent cooling of the waxy maize starch paste (WXSP) without MGM. With regard to the temperature of heating and cooling, the

Table 1. The influence of added monomyristin (MGM) on the rheological characteristics of starch pastes from native, hydroxypropyl potato starches and waxy maize starch

		Native potato starch	Hydroxypropyl potato starch (MS)			Waxy maize starch
			0·045	0·125	0·170	
G'	Control[a]	17·6	16·3	13·1	11·6	13·6
(Pa)	MGM[b]	225·0	131·0	25·2	18·2	46·8
G''	Control	8·7	7·6	6·6	6·1	8·7
(Pa)	MGM	19·2	18·0	8·9	8·6	19·7
δ	Control	26·1	27·6	28·3	30·2	39·8
(°)	MGM	4·9	7·8	19·4	25·3	22·8

[a]Without addition of MGM.
[b]With addition of MGM.

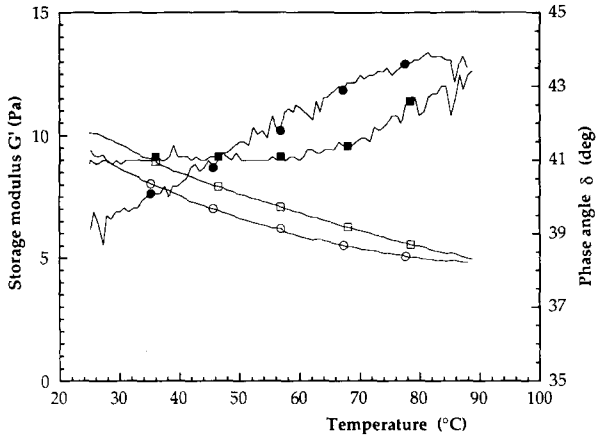

Fig. 2. Changes in storage modulus (G') and phase angle (δ) during heating and subsequent cooling of waxy maize starch paste. (□, G' heating; ○, G' cooling; ■, δ heating; ●, δ cooling.)

changes in both G' and δ were only small, and no abrupt changes in them could be seen.

The rheological behaviour during heating and cooling was altered, when 2·5% of MGM was added, as presented in Fig. 3. During heating of the waxy maize starch-MGM paste (WXSP-MGM), the initial level of G' began to decrease notably from about 35°C to about 55°C. The changes in G' during cooling were very similar to those during heating, with regard to the temperatures, although the level of G' during cooling was lowered. The δ during cooling decreased slowly, and became lower from about 65°C than that during heating.

These results showed that MGM gave rise to changes in rheological behaviour of WXSP mostly at the temperature range below about 65°C, and it is suggested that the association and dissociation of waxy maize starch and MGM then take place. This is well in accordance with electron spin resonance studies of waxy maize starch-fatty acids (Biliaderis & Vaughan, 1987; Pearce *et al.*, 1987).

Although the rheological transition occurred below 65°C, it could not be confirmed by DSC measurements (see Fig. 1). However, the results of the rheological measurements in our study suggest that there is an interaction between amylopectin and MGM. One reason why the WXSP-MGM did not show a more well defined rheological transition than the native potato starch-MGM paste, which will be described later, may be due to the molecular nature of amylopectin, which has a shorter chain length, and thus, a lower binding ability to MGM than the amylose.

Native potato starch. Figure 4 shows the rheological behaviour during heating and subsequent cooling of a native potato starch paste (NPSP), without MGM. As was the case for WXSP, no notable changes in G' and δ could be seen.

Figure 5 shows the rheological behaviour during

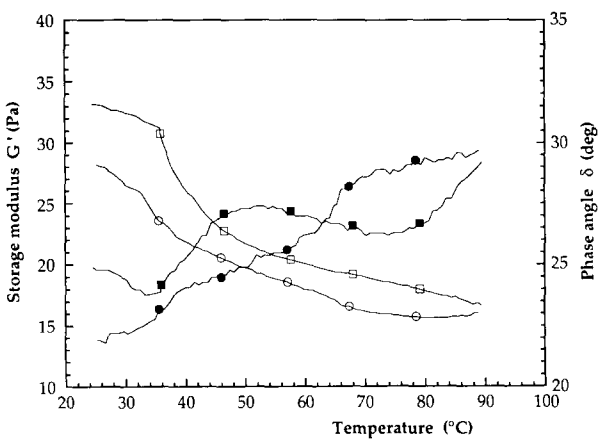

Fig. 3. Changes in storage modulus (G') and phase angle (δ) during heating and subsequent cooling of waxy maize starch-monomyristin paste. The legends are the same as in Fig. 2.

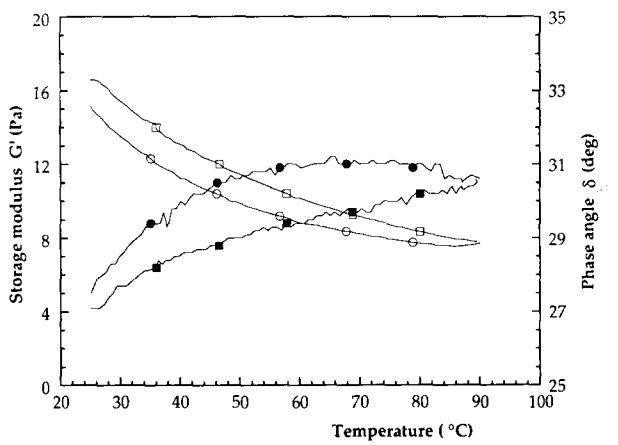

Fig. 4. Changes in storage modulus (G') and phase angle (δ) during heating and subsequent cooling of native potato starch paste. The legends are the same as in Fig. 2.

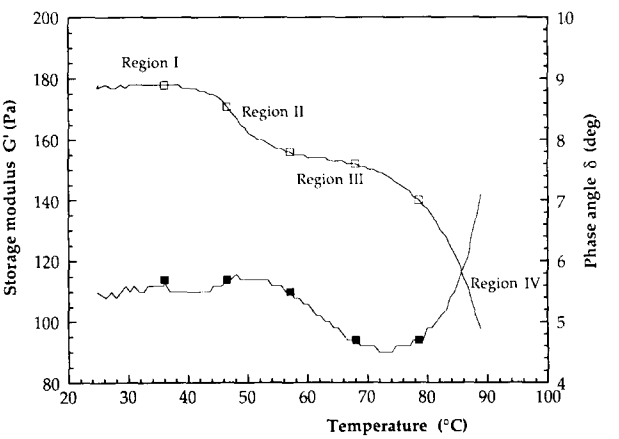

Fig. 5. Changes in storage modulus (G') and phase angle (δ) during heating of native potato starch-monomyristin paste. The legends are the same as in Fig. 2.

heating of the native potato starch-MGM paste (NPSP-MGM). Addition of MGM resulted in several changes in rheological behaviour.

In order to explain these changes, it is necessary, at this stage, to consider a possible gel structure of the NPSP-MGM. In potato starch, amylose constitutes about 25% and has been generally regarded as the component which forms inclusion compounds. Due to the cooking conditions used in this study, it is expected that the starch paste will consist of solubilized amylose and amylopectin in a continuous phase, in which more or less of the starch fractions and of the swollen starch granules are dispersed. When MGM is added, the amylose in the starch paste reacts with MGM and forms an amylose-MGM complex. The structure of the complex would be similar to that of the amylose-monostearin complex, proposed by Carlsson *et al.* (1979). Thus, the NPSP-MGM can be considered as a gel system where amylopectin may act as filler in the matrix of amylose-MGM complexes. The role of amylopectin in the gel system was suggested by the rheological behaviour during heating and cooling of the WXSP-MGM, previously described.

From Fig. 5, it is obvious that four different regions in the rheological behaviour of G' and δ during heating of the NPSP-MGM can be observed. The changes in G' and δ are interpreted, with regard to temperature, in the following way.

(1) Region I: the initial level of G' is maintained in the temperature range of about 25–45°C, indicating a stable region where no significant rheological changes occurred.

(2) Region II: the first notable decrease in G' occurs at about 46–58°C. In this temperature range, a slight increase in δ can be observed. This is the region for the first transition, which might be due to the dissociation of an interacted amylopectin-MGM within the amylose-MGM matrix of a gel system.

(3) Region III: a slight gradual decrease in G' occurs at about 58–76°C, which may be described as a plateau region. At this stage, the amylose-MGM matrix is stable while some changes in amylopectin-MGM continuously occur. The structure of the gel system becomes more and more elastic, as observed in the minimum value of δ at about 76°C.

(4) Region IV: from about 77°C, a second notable drop in G' occurred, accompanied by an increase in δ. The initial temperature of this region is very close to T_o of the endotherm of the mixture of gelatinized native potato starch-MGM (see Fig. 1). This region is the second rheological transition, which can thus be attributed to the thermal transition of the amylose-MGM complex, leading to its dissociation. The dissociation means that the amylose-MGM complex turns into the flexible-coil structure of the amylose, and thus it is expected that the amylose complex matrix in the starch-MGM paste has collapsed. This was observed as a sharp drop in G' with a marked increase in δ from about 77°C. At 90°C at the end of the heating, G' was about 65 Pa higher and δ was about 16·5° lower, than those of the NASP (control), suggesting that the gel system still contains undissociated complexes.

The rheological behaviour during the subsequent cooling of the heated NPSP-MGM is given in Fig. 6. As was the case during heating, there are also four different rheological regions in the changes of both G' and δ. During cooling, the increase in G' and decrease in δ are slow in the temperature range of 90–80°C, which may indicate that only a little complex formation takes place. From about 80°C, the increase in G' and the decrease in δ were very sharp until about 62°C. This region, leading to a more elastic structure, may be due mainly to the interaction between amylose and MGM. From about 62°C to 36°C, the second increase in G' was found. In this temperature range, a small increase followed by a decrease in δ can be seen. This may indicate that some kind of arrangements of fillers in the amylose-MGM matrixes are taking place, possibly between amylopectin and MGM. With further cooling, the NPSP-MGM became a very elastic structure with high G' and low δ values. The phase angle also showed four distinctive changes, corresponding to the changes in G'.

The G' and δ values of NPSP-MGM at 25°C, before heating and after subsequent cooling, differed considerably from each other. It indicates that a new structure of the gel system is created, resulting from dissociation and association of the starch and monomyristin.

Hydroxypropyl potato starches. Figure 7 shows the changes in the rheological behaviour during heating

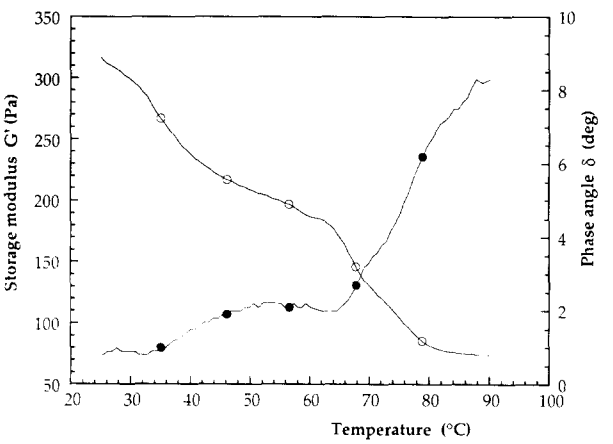

Fig. 6. Changes in storage modulus (G') and phase angle (δ) during cooling of native potato starch-monomyristin paste. The legends are the same as in Fig. 2.

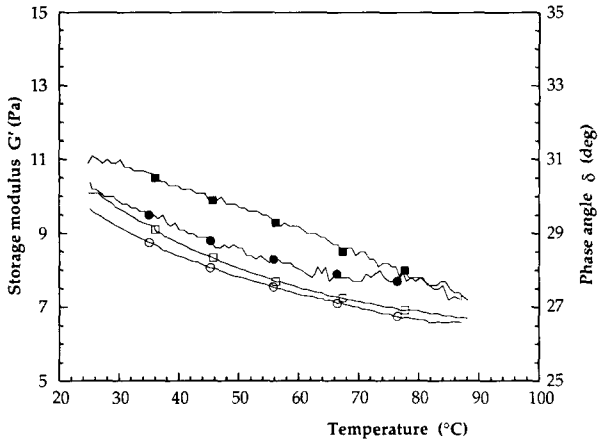

Fig. 7. Changes in storage modulus (G') and phase angle (δ) during heating and subsequent cooling of hydroxypropyl potato starch (MS 0·045) paste. The legends are the same as in Fig. 2.

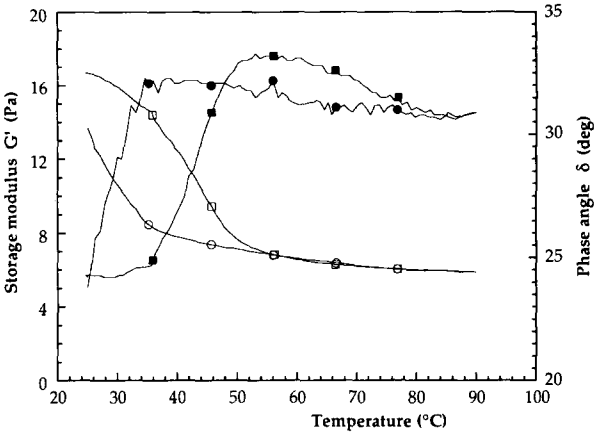

Fig. 9. Changes in storage modulus (G') and phase angle (δ) during heating and subsequent cooling of hydroxypropyl potato starch (MS 0·125)-monomyristin paste. The legends are the same as in Fig. 2.

and subsequent cooling of hydroxypropyl potato starch paste with MS 0·045 (H1SP), without addition of MGM. The results obtained from hydroxypropyl potato starches with MS 0·125 (H2SP) and MS 0·170 (H3SP) are not shown, since they were similar to those for H1SP. Only a slight change in G' and δ during heating and subsequent cooling was found in any of the hydroxypropyl starch pastes.

Figures 8–10 show the rheological behaviour during heating and subsequent cooling of hydroxypropyl potato starch (MS 0·045, 0·125 and 0·170)-MGM pastes (H1SP-MGM, H2SP-MGM and H3SP-MGM, respectively). The rheological behaviour was very different, depending on the MS of the starches.

During heating of the H1SP-MGM (Fig. 8), different regions were observed, as in the case of the NPSP-MGM (see Fig. 5). However, the plateau region (region III) in the NPSP-MGM was not present in the H1SP-

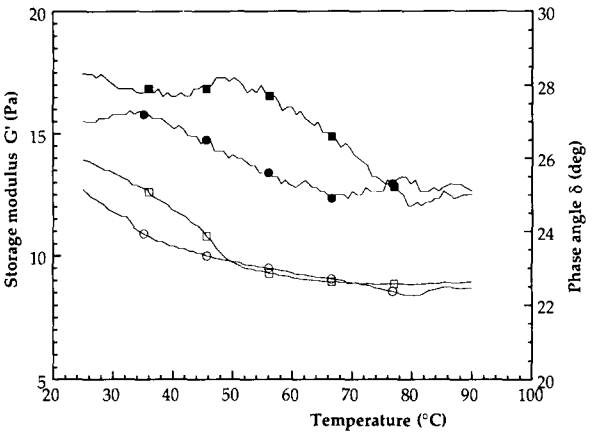

Fig. 10. Changes in storage modulus (G') and phase angle (δ) during heating and subsequent cooling of hydroxypropyl potato starch (MS 0·170)-monomyristin paste. The legends are the same as in Fig. 2.

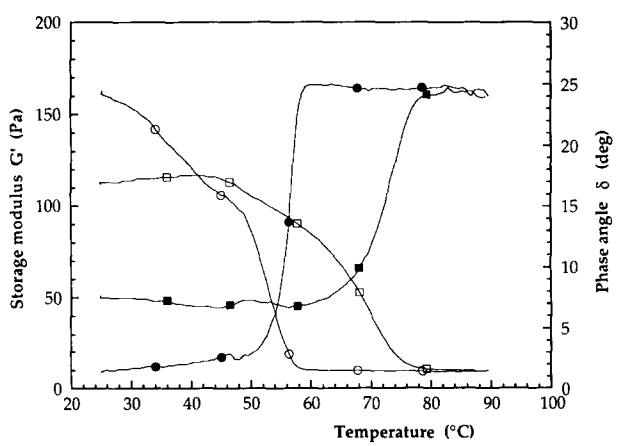

Fig. 8. Changes in storage modulus (G') and phase angle (δ) during heating and subsequent cooling of hydroxypropyl potato starch (MS 0·045)-monomyristin paste. The legends are the same as in Fig. 2.

MGM. From about 64°C, a sharp decrease in G' and an increase in δ began to occur, finishing at about 80°C, where the value of G' and δ reached almost the same as the H1SP (see Fig. 6). The temperature range of this region corresponded closely to that of the endothermic transition of the mixture of gelatinized hydroxypropyl potato starch (MS 0·045)-MGM (see Fig. 1). This further proved that the endothermic transition may be regarded as being due to the dissociation of the complex between MGM and amylose.

Cooling of the H1SP-MGM resulted in very different shapes in the G' and δ curves, compared to those during heating. The G' and δ maintained almost the same levels from 90°C to about 59°C, suggesting that no interaction took place. After this, a sharp increase in G' and decrease in δ occurred to about 48°C. These rheological changes may be due mainly to the formation of an amylose-MGM complex. A second increase in G'

was observed at about 47–33°C, and it could be due to an interaction between amylopectin and MGM.

This rheological evidence of the association and dissociation is further supported by electron spin resonance studies of interacted fatty acids–normal starches containing more than 20% amylose (Biliaderis & Vaughan, 1987; Pearce *et al.*, 1987). However, Biliaderis & Vaughan (1987) suggested that the association and dissociation of fatty acid–starch complexes during heating and cooling take place only for the incomplete complex between fatty acid and short chain segments of starch components, since the electron spin resonance spectra changes did not agree with DSC measurements of the corresponding system.

The H2SP–MGM (Fig. 9) during heating showed a slow decrease in G' from 30°C to 51°C, reaching almost the same value as the H2SP (without MGM, data not shown). However, the δ of the H2SP–MGM increased from about 38°C to 53°C. The temperature range is similar to that for the rheological changes of WXSP–MGM. When the H2SP–MGM was cooled, an increase in G' and a decrease in δ was found from about 38°C. When the MS increased to 0·170, a decrease in G' during heating of the H3SP–MGM also occurred to about 49°C. This is lower than H2SP–MGM, as shown in Fig. 10. The H3SP–MGM did not show a sharp increase in G' and δ did not drop during the whole cooling period, suggesting that almost no interaction took place.

The initial level of G' for H2SP–MGM and H3SP–MGM at 25°C before heating was not recovered after cooling. It is not clear whether these rheological changes are due to amylose, to amylopectin or to both of them.

The association (interaction) temperatures, as identified by a notable increase in G' during cooling, of the hydroxypropyl potato starches–MGM pastes, were different depending on the MS. They were also different from those of NASP–MGM and WXSP–MGM. The association temperatures were about 59°C and 80°C, respectively, for H1SP–MGM and NASP–MGM. For the other starch–MGM pastes, they were below 55°C. This may suggest that the physical state of MGM plays an important role in the interaction between MGM and the starches of different chemical and molecular nature. The concentration of MGM in the starch–MGM pastes was 0·25%, and at this concentration, it is known that MGM undergoes physical phase transitions (β-crystal, lamellar-liquid crystalline and cubic-liquid crystalline phases) with temperature. Above 85°C, the cubic phase exists (Riisom *et al.*, 1984), and no interaction take place, as observed even for the NPSP–MGM. The lamellar-liquid crystalline phase, which can be formed at about 60°C, is superior to the other phases for the association with starch (Larsson, 1983). This would be one of the reasons for the hysteresis in the changes of rheological properties of the starch–MGM paste, especially H1SP–MGM, occurring during heating and cooling. It is then expected that the interaction between H2SP and WXSP, respectively, and MGM would take place when the MGM was in the lamellar-liquid crystalline phase. However, for temperatures (below 55°C) the rheological response was delayed, possibly due to the molecular nature of these starches.

CONCLUSIONS

This study utilized the technique of dynamic rheological measurements to investigate the interactions between starches and MGM. The results have shown that the rheological behaviours of starch–MGM pastes were very different from each other, depending on the type of native starch and on the MS of hydroxypropyl potato starches. Also, the endotherms, measured by DSC, of the mixture of gelatinized starch–MGM differed. This may be due to the different ability of the starches to interact with MGM, resulting mainly from the chemical compositions and molecular structures of the starches.

The results of the rheological measurements suggested that there is an interaction between amylopectin and MGM, although the DSC measurement could not prove it. Furthermore, rheological evidence for the association and dissociation properties of the amylose–MGM complex was found from the rheological behaviour during heating and cooling of NASP- and H1SP–MGM. The temperature ranges for the dissociation closely corresponded to those for the endothermic transition, as measured by DSC, of the amylose–MGM complex. An association between starch and MGM pastes took place when they were cooled, creating a new structure of the gel system different from that before heating.

These results further suggest that the rheological properties due to association and dissociation of a lipid–starch complex can be properly directed by controlling the extent of the chemical modification of starch.

ACKNOWLEDGEMENT

Financial support was obtained from the Swedish Council for Forestry and Agricultural Research.

REFERENCES

Batres, L.V. & White, P.J. (1986). *J. Am. Oil Chem. Soc.*, **63**, 1537.

Biliaderis, C.G. & Vaughan, D.J. (1987). *Carbohydr. Polym.*, **7**, 51.

Carlsson, T.L.-G., Larsson, K., Dinh-Nguyen, N. & Krog, N. (1979). *Stärke*, **31**, 222.

Eliasson, A.-C. (1986). *Carbohydr. Polym.*, **6**, 463.
Eliasson, A.-C. & Kim, H.R. (1992). Changes in rheological properties of hydroxypropyl potato starch paste during evaluation of freeze–thaw stability *J. Texture Studies*, (in press).
Eliasson, A.-C. & Ljunger, G. (1988). *J. Sci. Food Agric.*, **44**, 353.
Goering, K.J., Jackson, L.L. & Dehaas, B.W. (1975). *Cereal Chem.*, **52**, 493.
Hahn, D.E. & Hood, L.F. (1986). *Cereal Chem.*, **64**, 81.
Hoover, R. & Hadziyev, D. (1981). *Stärke*, **33**, 290.
Kim, H.R. (1992). Unpublished data.
Kim, H.R., Hermansson, A.-M. & Eriksson, C.E. (1992). *Stärke*, **44**, 111.
Krog, N. (1973). *Stärke*, **25**, 22.
Larsson, K. (1983). In *Lipids in Cereal Technology*, ed. P.J. Barnes. Academic Press, New York and London, pp. 237–51.
Orthoefer, F.T. (1976). *Cereal Chem.*, **54**, 561.
Pearce, L.E., Davis, E.A., Gordon, J. & Miller, W.G. (1987). *Cereal Chem.*, **64**, 154.
Riisom, T., Krog, N. & Eriksen, J. (1984). *J. Cereal Sci.*, **2**, 105.
Takahashi, S. & Seib, P.A. (1988). *Cereal Chem.*, **65**, 474.