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Factors affecting the production of low-ester pectin gels

S.A. El-Nawawi*[a] & Y.A. Heikal[b]

[a]*Chemical Engineering Department, National Research Center, Dokki, Cairo, Egypt*
[b]*Food Engineering Department, Faculty of Agriculture, Ain Shames University, Cairo, Egypt*

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Low-ester pectin gels find wide application in food industries especially in low calorie or dietectic foods because of their low sugar content. They are also relatively stable during prolonged storage at room temperature and they retain their shape at higher temperatures. In the present work the factors affecting the production of low-ester pectin gels including pH, pectin, calcium and sugar concentrations were investigated. The purpose of the work was to obtain the optimum conditions for the production of gels of high firmness and strength with a range of elasticity and free from syneresis. Gel firmness and strength were measured over the ranges of pH 3–3·6, 15–100 mg Ca^{2+}/g pectin, 0·5–1·2% pectin and 10–50% sucrose. Conditions of pH (3, 3·6), (35, 45) mg Ca^{2+}/g pectin, 1% pectin and (20, 30%) sucrose were optimal for gel firmness and strength.

INTRODUCTION

Pectin gels produced from high-ester pectins (greater than 7% methoxyl) require acid conditions (near pH 3) and a high soluble solids content (65%) in order to produce satisfactory jelly. On the other hand, pectin gels produced from low-methoxyl (LM) pectin (3–6% methoxyl) are produced over a wide range of pH with or without addition of sugar in the presence of small portions of calcium (Doesberg, 1965; Nelson *et al.*, 1977). The amount of calcium present is very important. Too low a concentration results in weak gels which break or rupture during handling or transportation. Too much calcium on the other hand, causes brittle gels which often exhibit a tendency to weep or synergise. Gelled products with reduced solids content often have soluble solids near 30%, but calcium gelled products can be made having solids level below 10% or over 50% (Nelson, 1977). Variation in the nature of the low-ester pectin, in the buffer salts, in solids content and principally, in gel pH and level of added calcium will lead to varied gel textures (Kertesz, 1951; Nelson, 1977). The most notable textural deficiency is syneresis, a release of water from the gelled network. Syneresis is most often associated with low-ester pectin gels that can accept narrow or low levels of calcium (Nelson, 1977). Resilient low-solids gels that are not prone to syneresis or weeping are characterized by a high resistance to rupture when prepared under conditions that provide gels of similar sag characteristics. Gel texture is evaluated by measuring both gel strength (resistance to rupture) and gel power (resistance to sag). When the ratio of gel strength to gel power is larger than one, the gel is less prone to syneresis, displays a continuous elastic texture and smooth fracture planes. As the gel strength to gel power ratio drops below one, a gel tends to be brittle, of grainy texture and prone to syneresis.

* To whom correspondence should be addressed.

EXPERIMENTAL

Sample preparation

Low-methoxyl citrus pectin ammonia which was demethylated and having a methoxyl content of 5·6% was prepared according to the method previously investigated (El-Nawawi & Shahata, 1987; El-Nawawi & Heikel, 1993). The ammonia de-esterification procedure was conducted at 25°C with 1 N NH_4OH in isopropanol solution. This reaction was stopped after 12 h by neutralization to pH 4 with 6 N HCl. The acid precipitated pectins were washed several times with 60% ethanol until free of NH_4Cl, followed by final washing with 95% ethanol and acetone before air drying.

Pectin analysis and gel evaluation

Moisture, ash, galacturonic acid content and methoxyl content were determined according to the methods

described in Raganna (1977) and molecular weight was determined by the method of McCready (McCready, 1970). Amide content was determined by the method described by Kim *et al.* (1978*a*). The percentage of free carboxyl groups was calculated by subtracting % esterification and % acid amide groups from total galacturonic acid content. Standard test gels were prepared by the National Research Council procedure using 1% pectin, 30% sucrose, 25 mg Ca^{2+}/g pectin and a pH of 3·0. The procedure allowed systematic variation of pectin content, dissolved solids level, calcium level and gel pH. The prepared gels were evaluated by measuring both gel firmness and gel strength. Gel firmness determination by a sag measurement (Natl Acad. Sci., 1972), similar to the procedure used to grade high methoxyl (HM) pectins gels reflects the ability to form gel. Gel strength, determined by measuring the force needed to rupture gel slices (Nelson, 1977), reflects the elasticity of the gel.

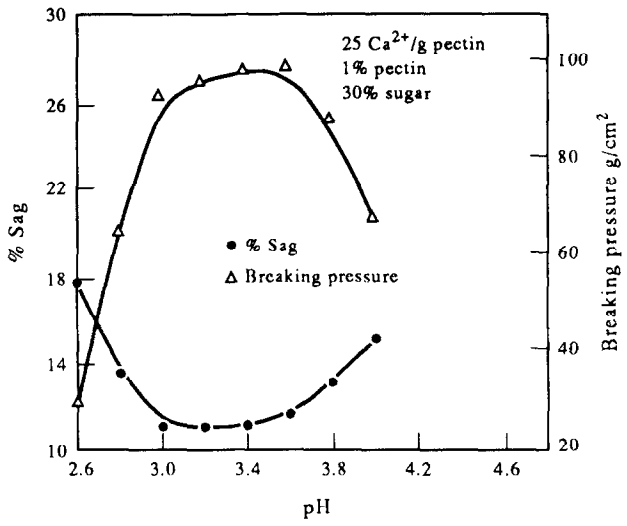

Fig. 1. Effect of pH on the gelation characteristics.

RESULTS AND DISCUSSION

The ammonia-demethylated citrus pectin used has an ester content of 34%, amide content of 11%, free carboxyl group content of 46%, galacturonic acid content of 91%, and molecular weight of 100×10^3 on an ash and moisture-free basis.

Effect of pH

The gelation characteristics of citrus pectin gels over a pH range of 2·6–4 with concentrations of calcium, sugar and pectin being kept constant at each pH are shown in Fig. 1. The least degree of sag for the citrus pectin gel occurred at a pH range of 3–3·4 and maximum breaking pressure was at pH 3·6. These results differ slightly from those of Black and Smit (1972) who obtained the maximum breaking pressure at pH 3·8 and minimum sag at pH 3·3–3·7. Their commercial citrus LM pectin contained 33·7% ester groups, 13% amide groups and 49·4% free carboxyl groups. For a LM pectin of 32% esterification, Doesberg (1965) showed an increase in gel strength measured as a compression modulus of elasticity, from pH 2·4 to 3·1, followed by a gradual decrease. Owens *et al.* (1949) measured gel strength as the shear modulus for an acid demethylated LM pectin which contained 21·5% ester groups and no amide groups. They reported that the maximum gel strength occurred at pH 2·7, with values decreasing on either side of this pH. Nelson (1981) reported that for commercial LM pectins maximum gel power occurs near pH 3 while gel strength peaks at slightly higher pH. As pH increases, both gel strength and gel power begin to decline. They used LM pectin of 39% esterification and 17% amidation. It is generally accepted that gelation characteristics to an extent are determined by hydrogen and calcium bonding, and are associated with the proportions of methoxyl, amide and free carboxyl groups as well as their distribution on the polygalacturonic acid molecules. It was observed that increasing the gel pH from 2·6 to 3·1 improved the gel strength, elasticity, smoothness and uniformity of the texture. At pH 2·6 and lower the gels were soft, granular and lacked clarity. This phenomenon may be a result of the partial precipitation of citrus pectin in low pH gels, thereby providing insufficient free carboxyl groups for calcium ions to form the framework of a gel. It has also been found that the increasing acidity, samples were more difficult to dissolve and become more viscous. This result supports the conclusion reached by Doesberg (1965) that viscosity of low-ester pectin solutions varies with changes in pH, and that association between molecules and precipitation occurs below pH 4. At pH 3·1–3·4 the pectins were more soluble and showed less tendency for pregelation during preparation. Kim *et al.* (1978*b*) and Sosulski (1978) had also found that pregelation and brittleness of the gel were greatly reduced as the pH was increased and that gels tended to break and collapse at low pH values. LM pectins can be used in products varying in pH from 2·5 to 6·5 (Anon, 1947). However, a maximum breaking pressure reading was obtained at pH 3·6 and a minimum of sag was obtained at pH 3–3·4. Although the observation of an optimum pH for maximum gel strength for a given pectin under given conditions is found frequently in the literature, no explanation for the observation has been given. The calcium sensitivity of the pectin, as well as the chelating power of citrate will change with increasing pH and this may be responsible for the optima observed (Black & Smit, 1972).

Effect of pectin concentration

The data presented in Fig. 2 were obtained with the standard gel formula in which only the pectin concentration was varied while the other conditions were

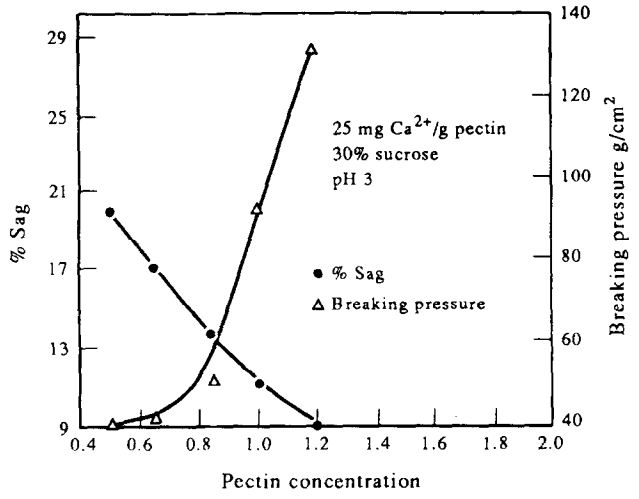

Fig. 2. Effect of pectin concentration on the gelation characteristics.

maintained at pH 3, 30% sugar and 25 mg Ca^{2+}/g pectin. The amount of calcium was adjusted to keep the calcium : pectin ratio constant. The percent sag decreased almost linearly as the pectin concentration increased from 0·5 to 1·2%. A linear relationship was also found between breaking pressures and pectin concentration. This can be attributed to the presence of more free carboxyl groups for calcium ion linkage through which pectin chains were held together, forming a strong gel (Anon, 1970; Black & Smit, 1972). Owens *et al.* (1949) found for a LM pectin used with a constant calcium : pectin ratio of 40 mg/g, that increasing the pectin concentration increased the gel strength as a logarithmic function, where strength was measured as the shear modulus by the rigidometer. Black and Smit (1972) reported that at a constant calcium level, there was linear relationship between the sag distance and certain concentrations of pectin gels. A similar relationship was also observed by Sosulski *et al.* (1978) in their work with citrus and sunflower head pectin gels, using 25 mg Ca^{2+}/100 g gel. They found that the percent sag was directly proportional to pectin concentration in the range 0·55–0·75/100 g of both gels. Kim *et al.* (1978*c*) showed for a sunflower pectin used with a constant calcium : pectin ratio of 25 mg/g, that the percent sag decreased linearly as the pectin concentration increased from 0·75 to 1·25%. They found in their investigation also that the sunflower pectin had a high rate of increase in gel strength. The increment in breaking pressure with increase in pectic concentration between 0·875 and 1·25% was 198·4 g/unit. percentage of pectin. They attributed this to the large proportion of free carboxyl groups present, as the sunflower pectin they used had 69·1% free carboxyl groups. It is important to stress that the data reported here were obtained with one pectin preparation. The calcium sensitivity of a low-ester pectin is dependent on a variety of factors such as the presence of amide groups in the pectin, methods used during pectin manufacture, the solids content of the gel etc. As a result, somewhat different results may be expected with other pectin preparations. It has been found in this investigation that, at low levels of pectin, gels showed improvement in both brittleness and pregelation, however, the gels were very weak in both firmness and strength. On the other hand, the gels containing 1·2% pectin were too firm and strong and showed severe brittleness. Therefore, 1% pectin was used for further studies of the effect of sugar and calcium concentrations on gel properties.

Effect of soluble solids

Figure 3 demonstrates the effect of varied soluble levels in the range of 10–50% at pH 3 and 3·6. At pH 3, an increase in the soluble solids level from 10 to 20% has little influence on gel texture: both gel strength and firmness increased slightly. As the level

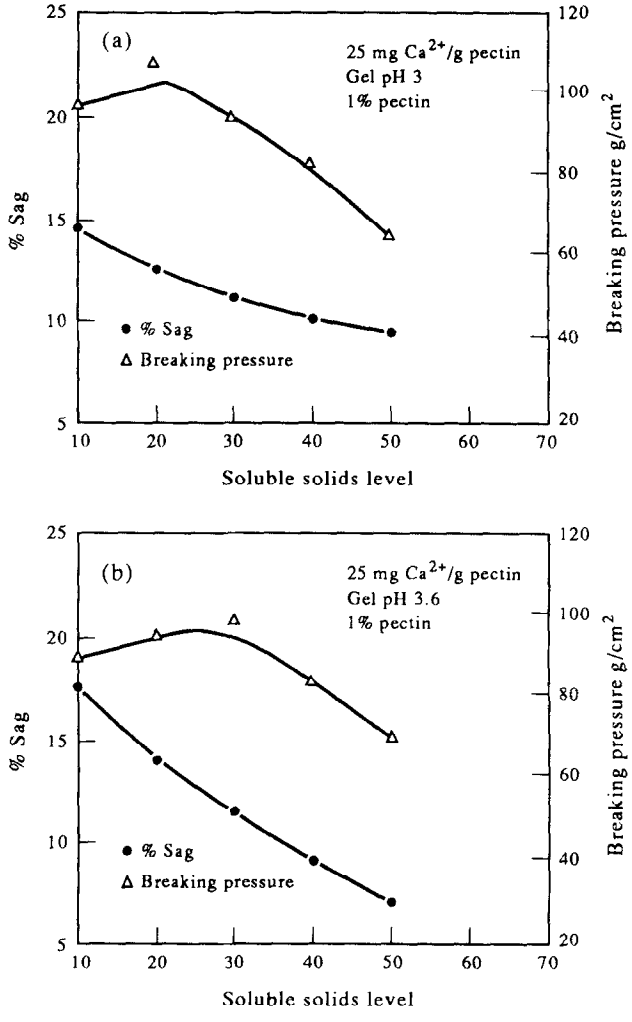

Fig. 3. Effect of soluble solids level on the gelation characteristics.

of soluble solids exceeds 20%, gel strength drops sharply while gel firmness increases slightly leading to a weak gel that fractures in an irregular fashion and is prone to syneresis. At pH 3·6, an increase in soluble solids level in the range of 10–30% leads to a slight increase in gel strength, but gel firmness increases markedly. As the soluble solids level exceeds 30%, gel strength decreases while gel firmness continues to increase leading to a weak gel which is brittle, coarse and prone to syneresis. It has also been found that gels obtained at pH 3·6 are weaker than those obtained at pH 3·0 for a soluble solids levels range 10–40%, above 40% the gel texture i.e. gel strength and gel firmness are less pH-dependent. These results differ slightly from those of Nelson (1977), who obtained a weak gel of gel strength to gel power ratios of below one for soluble solids levels above 22% at a pH of 3 and for soluble solids levels above 30% at pH 3·45. He also found that above 40% soluble solids levels gel strength and power are less pH-dependent. Sosulski (1978) reported that at a given pH, the citrus pectin formed a firmer gel at higher sucrose levels. He found that at 20 and 30% sucrose content, the citrus pectin gels had a maximum gel power at pH 2·9–3·0 and became weaker at pH values over 3. He determined the maximum gel power of the 40% sucrose level at pH 3–3·3 and also found that the gel power above this sugar level (40%) was less pH-dependent than that at 20 and 30% sucrose levels.

Effect of calcium

Figure 4 shows the changes in sag and breaking pressure with increasing calcium : pectin ratios. The calcium level ranged from 15–100 mg/g pectin at pH 3 and pH 3·6. The pectin and sugar concentrations were kept constant at 1 and 30% respectively. There is much evidence in the literature (Pilnik & Voragen, 1970) that gel formation is not merely due to 'bonding' through primary valencies but that secondary valencies between calcium and hydroxyl groups play an important role. From Fig. 4, as the calcium level increased from 15 to 100, the degree of sag decreased linearly to at least the 65 mg level for gels prepared at pH 3·0 and to the 55 mg level for gels prepared at pH 3·6. The gel strength at pH 3·6 increased more sharply than that at pH 3·0 reaching a maximum at 35 mg Ca^{2+}, while a maximum strength was reached at 45 mg Ca^{2+} and pH 3·0. Nelson (1981) reported on the effect of varied calcium content in the range of 20–45 mg Ca^{2+}/g of pectin on the gel strength and gel power for a commercial LM citrus pectin. He found that the gel texture was not sensitive to the calcium levels used in his investigation at pH 3·0. However, the calcium sensitivity became more pronounced for gel pH near 3·5. At calcium levels above 35 mg/g of pectin he obtained a weak gel of gel strength to gel power ratio below one. Sosulski

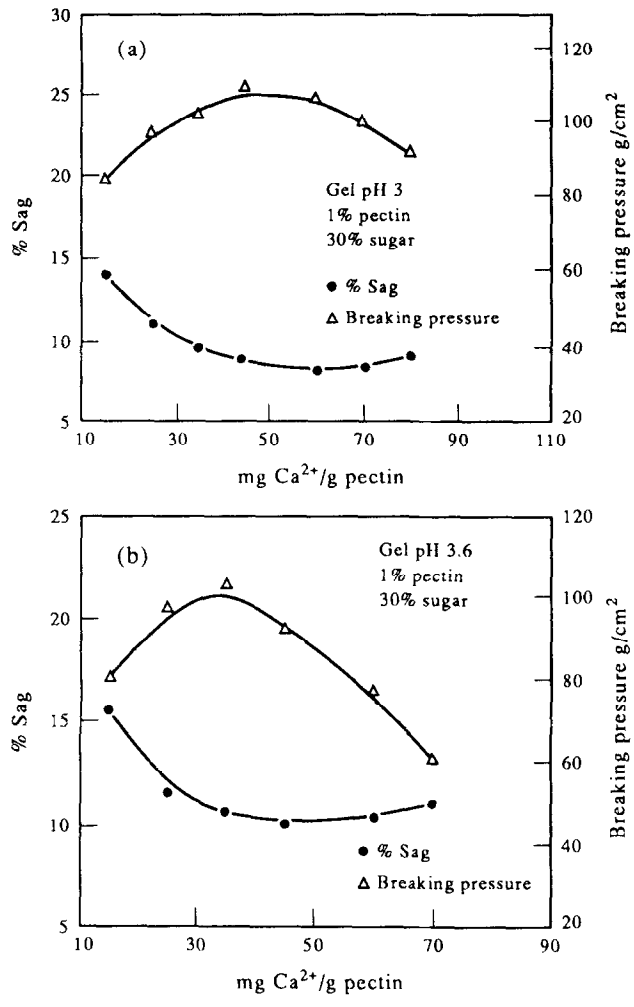

Fig. 4. Effect of calcium level on the gelation characteristics.

(1978) reported on LM citrus pectin gels containing 30% sucrose and four calcium levels (20, 25, 30, 35 mg/g of pectin). He found that the citrus pectin was not sensitive to the calcium levels used in this study between pH 2·6 and 3·2 but above this pH range, the calcium sensitivity become more pronounced as the pH increased. At all calcium levels, citrus pectin gels collapsed below pH 2·5 and the 35 mg Ca^{2+} collapsed above pH 3·3. Black and Smit (1972) obtained a sharp decrease in sag over a wide range of calcium content from 22·5 to 60 mg for low-ester citrus pectin which contained 13 amide groups/100 galacturonic acid units. They obtained a maximum strength value at 40 mg calcium level and a minimum sag at around 60 mg Ca^{2+}/g of pectin. Hills *et al.* (1949) also obtained maximum strength values decreasing on either side of a certain optimum calcium level, when calcium level was plotted against jelly strength as measured by a Delawave jelly tester. From Fig. 4 at low calcium levels i.e. 20 mg Ca^{2+}/g pectin, gels had high sag and low breaking pressures showing a lack of sufficient calcium. Low strengths at high calcium levels appear to result from difficulties in obtaining a uniform calcium–pectin

dispersion (Owens *et al.*, 1949). In this case, pregelation often occurs resulting in an unevenly formed and weak gel. Increasing the calcium level resulted in a sharp decrease in sag. Sag still decreased and a minimum was obtained at around 65 mg Ca^{2+} for pH 3 and 55 mg Ca^{2+} for pH 3·6, despite the fact that slightly less than 45 mg Ca^{2+}/g pectin at pH 3·0 and 35 mg Ca^{2+}/g pectin at pH 3·6 would have been sufficient to bind all the available carboxyl groups. The slight increase in sag at very high calcium levels is probably due to the extreme pregelation which occurs under those conditions (Black & Smit, 1972). However, the gel strength of the present citrus pectin gels was more sensitive to calcium at levels lower than 35 mg. In low-ester citrus pectins having 25–35% esterification, calcium levels for maximum gel strengths were 40 mg for NH_4 de-esterified pectin amide (Black & Smit, 1972), 40–60 mg for acid treated pectins (Owens *et al.*, 1949) and 17–20 mg for enzyme demethylated pectin (Hills *et al.*, 1949). The low-ester pectin demethylated by pectin esterase is believed to have a non-random distribution of methoxyl groups which decreases sensitivity to calcium ions and results in poor gel strength (Hills *et al.*, 1949; Speiser & Eddy, 1946).

CONCLUSION

The low-ester citrus pectin gels investigated when evaluated in varied pH gels having about 30% soluble solids, show a steady decline in gel strength and gel power as the pH increases from 3, a pH used for low-ester pectin gels grading, to pH 3·6 and above. Gelling ability and resistance to rupture are lowered in the pH range of end use, i.e. pH 3·0–3·6. This behaviour is further compounded by the increased sensitivity of gel strength to higher calcium levels in the pH range of end use. The decrease in gel strength brought about by increased calcium is promptly manifested as syneresis. To some extent, the decrease in gel strength by increased calcium can be overcome by a low-ester pectin of higher molecular weight as discovered by Wiles & Smit (1946). In addition, when compared with gels having 30% soluble solids the 40% and 50% soluble gels prepared with the investigated low-ester pectin show a distinct loss in gel strength. Hence, the investigated low-ester pectin gels suffer loss of gel resilience and are prone to syneresis in end use applications where varied conditions of pH, calcium concentration and solids content do not allow the formation of gels having desirable textural properties.

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