Electronic Supplementary Information

Multiscale structural and rheological features of colloidal low-methoxyl pectin solutions and calcium-induced sol-gel transition

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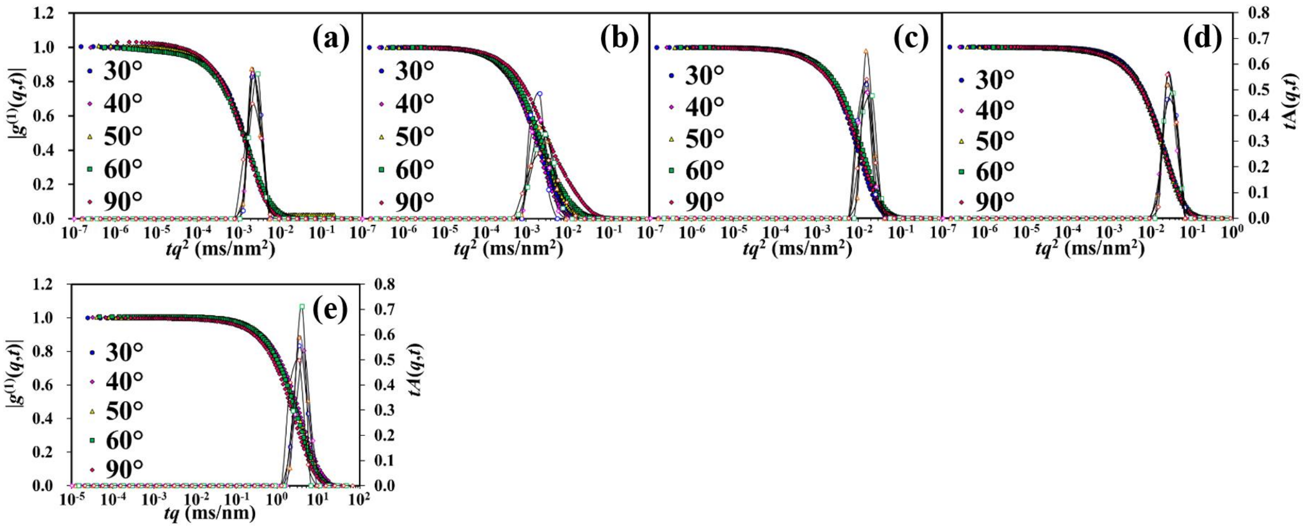

Fig. S1 DLS features of pectin solutions with filtration treatment for the whole solution. The nominal concentrations prior to the filtration are (a) 0.1, (b) 0.5, (c) 1.0, (d) 1.5 and (e) 2.0 wt.%. The corresponding mean hydrodynamic radii are R_h = 600, 900, 4400, 8000 nm, respectively, for the first four solution samples that exhibit the usual diffusional behavior. The results clearly suggest that colloidal agglomerate species can be reformed even after the filtration treatment.

Fig. S2 Photographs showing the outer appearance of (a) the original and (b) filtered pectin solutions at various concentrations: 0.1, 0.5, 1.0, 1.5, and 2.0 wt.%.

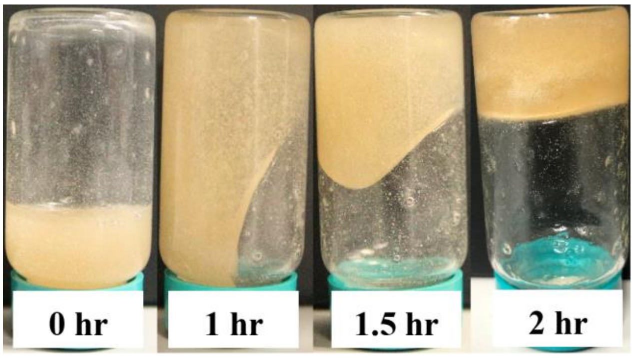

Fig. S3 Photographs showing the results of flow experiment during LM pectin/Ca^{2+} sol-gel transition.

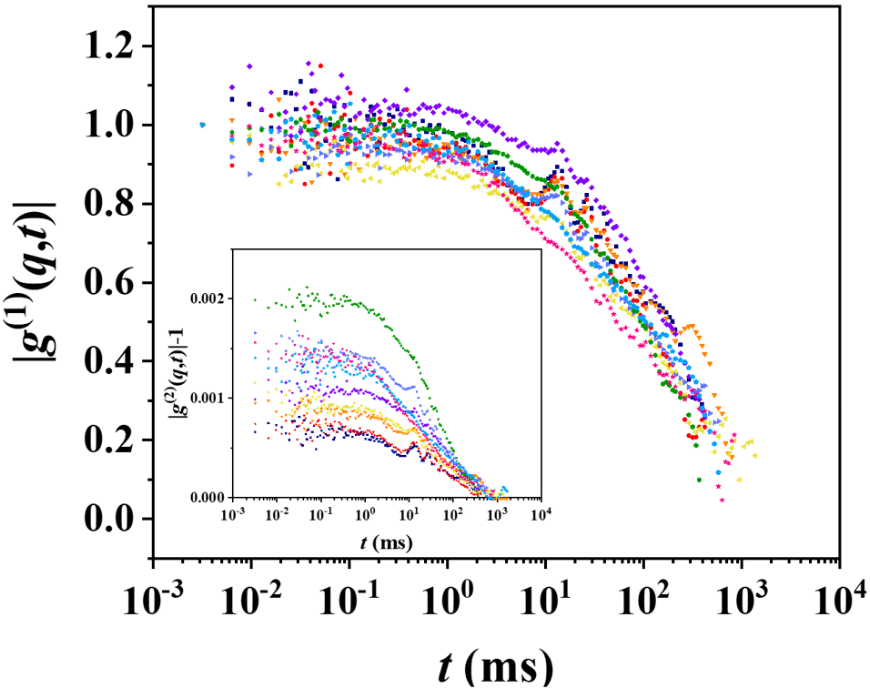

Fig. S4 DLS features obtained from scanning of the LM pectin/Ca^{2+} gel at various sample positions.

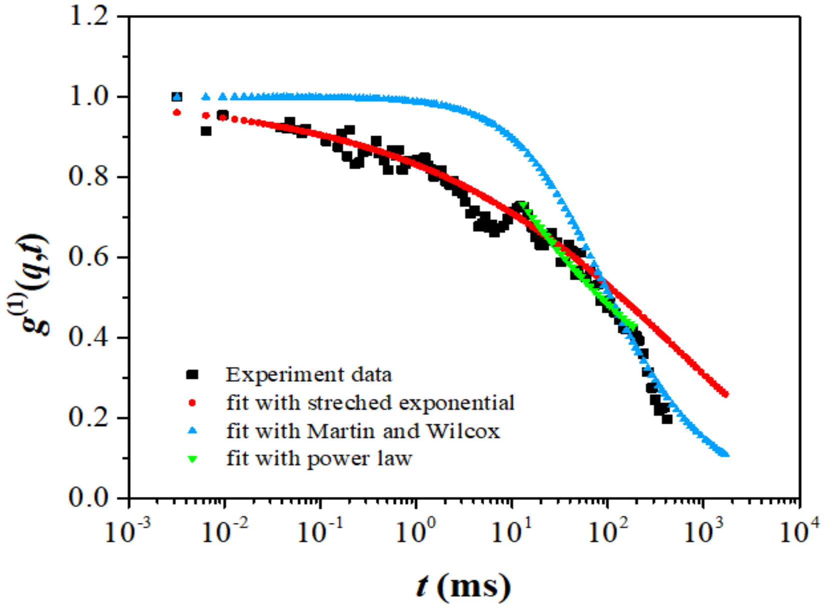

Fig. S5 DLS data on the LM pectin/Ca^{2+} gel and model fits using the stretched-exponential function (red): $|g^{(1)}(q,t)| = \exp[-(t/\tau)^{0.26}]$, the power-law part of Martin-Wilcox theory (blue): $|g^{(1)}(q,t)| = \{[1+(t/t^*)]^{(n-1)/2}\}^2$, $n = 0.36$, and the power-law model (green): $|g^{(1)}(q,t)| = 1.24\,(t)^{0.20}$, respectively.

Model fits of SALS/SLS/SAXS data:

Pectin solutions. To describe the scattering data in Fig. 5 that mark the interior mass-fractal structure of an agglomerate species formed by individual rod-like (or worm-like) pectin chains, the following formulation that combines form and structure factors was utilized:

$$I_{\mathrm{agglomerate}}(q) = k\, S_{\mathrm{fractal}}(q)\, P(q) \tag{S1}$$

where k is a scale factor. Semiflexible chains free from the effects of excluded volume can be described by the following expression for the case with L/b>2:[1-3]

$$P(q,L,b,r) = K_{\mathrm{chain}} \cdot P_{\mathrm{chain}}(q,L,b) + K_{\mathrm{rod}} \cdot q^{-1} \frac{J_1^{\,2}(qr)}{(qr)^2} \tag{S2}$$

$$P_{\mathrm{chain}}(q,L,b) = \{P_{\mathrm{SB}}(q,L,b)\}\exp\left[-((qb)/q_1)^{p_1}\right] + P_{\mathrm{loc}}(q,L)(1 - \exp\left[-((qb)/q_1)^{p_1}\right]) \tag{S3}$$

where

$$P_{\mathrm{SB}}(q,L,b) = P_{\mathrm{Debye}}(q,L,b) + \left[\frac{4}{15} + \frac{7}{15u} - \left(\frac{11}{15} + \frac{7}{15u}\right)\exp(-u)\right] b/L$$

$$P_{\mathrm{loc}}(q,L) = \frac{1}{Lbq^2} + \frac{\pi}{Lq}$$

$$P_{\mathrm{Debye}}(q) = \frac{2}{u^2}\left[\exp(-u) - 1 + u\right]$$

$$u = q^2 R_g^2 = q^2(bL/6)$$

In the above equations, L is the contour length, b is the Kuhn length, q_1=5.53, p_1=5.33, K_{chain} and K_{rod} are used to describe the contributions from the bulk polymer chain and local rod-like segment, respectively, and r is the rod radius.

For the structure factor in eqn (S1), a rather general expression describing the mass-fractal network was utilized:[4]

$$S_{\text{fractal}}(q) = 1 + \frac{D_{\text{m}}\Gamma(D_{\text{m}}-1)\sin[(D_{\text{m}}-1)\tan^{-1}(q\zeta)]}{(qr_0)^{D_{\text{m}}}(1 + 1/(q\zeta)^2)^{(D_{\text{m}}-1)/2}} \tag{S4}$$

where D_{m} denotes the mass-fractal exponent (or dimension) of an agglomerate species, ζ represents the cut-off distance where the mass-fractal structure ceases to apply, and r_0 ($\approx R_{\text{g,chain}}$) denotes the dimension of the constituting chains. The full set of fitted parameters is given in Table 1.

Pectin/Ca^{2+} sol-gel. The combined scattering intensity profile shown in Fig. 10 can be divided into two different regions: the agglomerate region at low q and the aggregate region at higher q (> 0.001 nm^{-1}):

$$I(q) = I_{\text{agglomerate}}(q) + I_{\text{aggregate}}(q) \tag{S5}$$

The first contribution, $I_{\text{agglomerate}}(q)$, is described by the Guinier–Porod model for three-dimensional objects:[5]

$$I_{\text{agglomerate}}(q) = G \exp\left(\frac{-q^2 R_{\text{g,agglomerate}}^2}{3}\right), \quad \text{for } q \leq q_1 \tag{S6}$$

$$I_{\text{agglomerate}}(q) = \frac{B}{q^{D_{\text{m,agglomerate}}}}, \quad \text{for } q \geq q_1$$

$$q_1 = \frac{1}{R_{\text{g,agglomerate}}}\left(\frac{3D_{\text{m,agglomerate}}}{2}\right)^{1/2}$$

where G and B are two scale factors, and $D_{\text{m,agglomerate}}$ denotes the mass-fractal exponent for the agglomerate species.

The second contribution from the aggregate species that constitutes an agglomerate, $I_{\text{aggregate}}(q)$, can be further divided into three terms: the mass-fractal structure of an aggregate, the form factor of the constituting cylindrical bundle, and the mesh structure of a bundle formed by individual rod-like chains:[6]

$$I_{\text{aggregate}}(q) = kS_{\text{fractal}}(q)P_{\text{cyl}}(q) + I_{\text{P}}(0)P_{\text{cyl}}(q) + \frac{I_{\text{D}}(0)}{[1+q\zeta_{\text{d}}\exp(q^2r^2/4)]} \tag{S7}$$

$$P_{\text{cyl}} = \int_0^{2\pi} \left(\frac{\sin(\frac{qL}{2}\cos\varphi)2J_1(qR\sin\varphi)}{(\frac{qL}{2}\cos\varphi)(qR\sin\varphi)} \right)^2 \sin\varphi \, \text{d}\varphi$$

where k, $I_{\text{P}}(0)$, and $I_{\text{D}}(0)$ are three scale factors, R (=1/2 d) and L denote the radius and length, respectively, of randomly packed cylinders (bundles), ζ_{d} and r denote the mean mesh size and radius, respectively, of the constituting rod-like chains within a bundle. The full set of fitted parameters is given in Table 2.

References

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