Using DLS-Microrheology and Raman Spectroscopy to probe self-assembly and gelation mechanisms in complex fluids

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ABSTRACT

Complex fluids are of great interest for in providing structure to a vast amount of materials in our daily environment, like processed foods, personal care products household detergents This paper describes the simultaneous determination of rheology as DLS- microrheology and high resolution Raman spectroscopy to investigate the mechanisms for the conformational changes needed to give the products a desired rheology.

INTRODUCTION

Complex fluids such as biopolymers, protein dispersions and surfactants play a critical role in providing both functional and sensory benefits in many processed foods and personal care products. The process of self-assembly in these complex materials and their associated rheological response needs to be engineered to provide stability, texture and any additional functional benefits. Controlling such behaviour requires manipulation of the micro/ mesostructure often by controlling the extent of intermolecular/intramolecular associations and interactions between components[1].

Most insights into the self-assembly process and the corresponding changes in rheological behaviour have primarily focused on elucidating micro/ mesostructural changes through various scattering (light, x-ray, neutron) and imaging techniques (cryo-TEM, SEM, AFM). Furthermore detailed insights into the associated chemical conformational/molecular structural changes and various non-covalent interactions (e.g. H-bonds, hydrophobic interactions) leading to the self-assembly process have been very limited. An understanding of the molecular level structural changes as self-assembly and gelation progresses can provide new mechanistic insights that can assist the formulation development process.

The talk will show how the combination of mesoscale structure-property elucidation techniques such as DLS/optical microrheology combined with high resolution chemical structure/conformation elucidation techniques such as Raman Spectroscopy can generate novel mechanistic insights for complex fluids and soft matter systems that are commonly encountered in food and personal care applications. This will be exemplified through studies into the self-assembly/gelation mechanism in a thermo-reversible gel forming agarose, a widely utilized food protein-β-lactoglobulin undergoing temperature induced aggregation/self-assembly[2] and the influence of salt concentration on a worm-like micelle system[3].

METHODS

DLS- microrheology

DLS or Dynamic light scattering is a common technique for the determination of particle size of submicron particles by using the Stokes equation (Eq. 1) and entering the viscosity of the continuous phase the hydrodynamic diameter can be determined.

$$d(h) = \frac{kT}{3\pi\eta D} \quad (1)$$

By using particles of a known diameter, probe or tracer particles, the DLS correlation function, $g^1(\tau)$ can be correlated to the mean square displacement of the particle from its Brownian motion (Eq. 2)

$$g^1(\tau) = g^1(0)\exp\left(-\frac{1}{6}q^2\left\langle\Delta r^2(\tau)\right\rangle\right) \quad (2)$$

where q is the magnitude of the sqattering vector (Eq. 3)

$$q = 4\pi n \sin(\theta/2)/\lambda \quad (3)$$

with n being the refractive index of the solvent, λ the wavelength of light and θ the scattering angle, $g^1(0)$ is the value of the correlation function or intercept at zero time, theoretically 1. This value is commonly lower due to optical effects. Eq. 2 above is only valid in the single scattering regime. The complex shear modulus G(s) can be obtained through a unilateral Laplace transform of the MSD using a generalized Stokes-Einstein relationship. The G(s) is converted into the complex modulus in the frequency domain by an estimation method developed by Mason[4] (2000).

Raman Spectroscopy

Raman spectroscopy is a using the inelastic scattering of light from a diode laser at 785 nm (≈ 280mW) that is sensitive to bending and stretching of bonds, but since only 1 in 1000000 photons is Raman scattering is a technique that is useful for water based systems in higher concentrations. Amide and aromatic side chains are Raman active and environmental changes that affect these bonds will give information about secondary and tertiary structure. The Raman spectrophotometer characterizes materials from inter and intra molecular structure, backbone configuration, side chain orientation, hydrophobic or hydrophilic environment and the hydrogen bonding.

Zetasizer Helix

The Zetasizer Helix (fig. 1) is an instrument that simultaneously measures on the same sample at the same time for the same temperature to give to give twofold information about hydrodynamic size, interaction parameter, rheology and colloidal stability from DLS/ DLS-microrheology. The Raman side gives information about secondary/ tertiary structures and conformational stability

Figure 1. The Zetasizer Helix

EXAMPLES

Aggregation of biopolymers (agarose)

Agarose solutions (0.2, 0.5 and 1% w/v) is measured in a Zetasizer Helix to determine the mechanism of the gelation as function of temperature. Fig. 2 shows the DLS-microrheology data with decreasing tem-perature and fig. 3 shows the Raman spectra close to the aggregation temperature indicated from the DLS-microrheology. Fig. 4 shows the combined data of the storage

modulus, G', from microrheology and the integrated intensity between 140-200cm-1 with decreasing temperature.

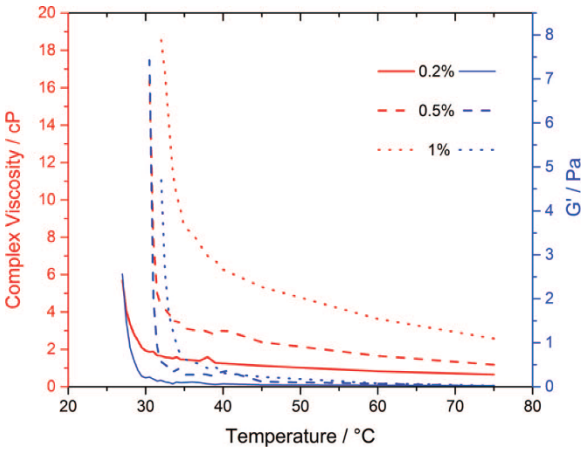

Figure 2. Complex viscosity, η*, and storage modulus G' elastic as function of temperature for 0.2, 0.5 and 15 w/v agarose solution.

Fig. 2 indicates that the aggregation temperature is shifted towards slightly higher temperatures as concentration is increased.

Fig 3. Raman spectra shows an increase in intensity at 170 cm^{-1} as temperature is reduced. The peak at 170 cm^{-1} shows the relative intensity of hydrogen bonding

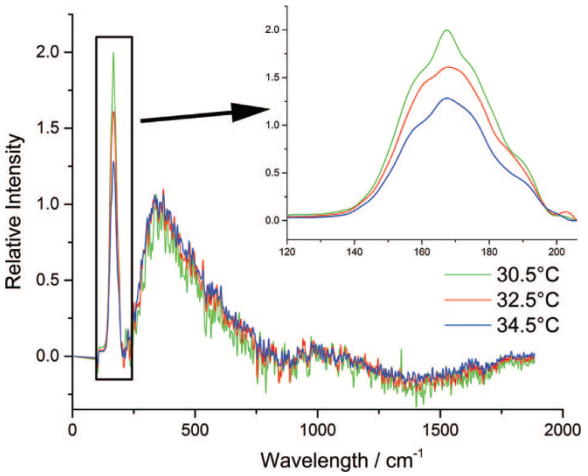

Figure 3. Raman spectrum for 0.5% agarose solution as function of temperature. Insert is zooming in on intensity around 170cm^{-1} as temperature is decreased.

The increase in intensity is attributed to the increasing number of water molecules confined in the structure upon cooling.

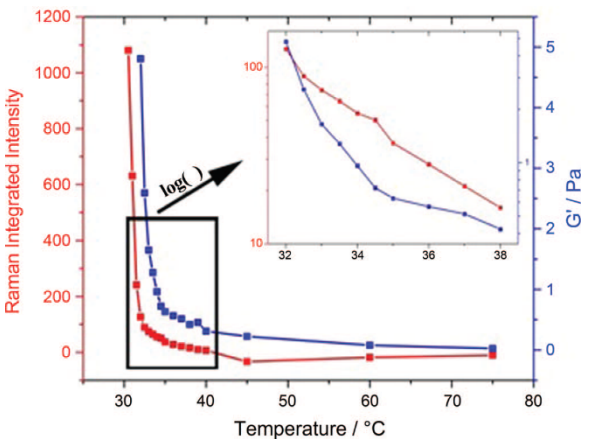

Figure 4. Raman integrated intensity (between 140- 200 cm^{-1}) and G' as function of temperature

Fig. 4 shows a very good agreement between the water absorption and elasticity increase and therefore it's indicating that there is an increased confinement of water molecules during the gelation process.

Protein stability (β-lactoglobulin)

Aggregation of β-lactoglobulin as function of temperature is shown in fig. 5 showing the complex viscosity and z-average particle diameter.

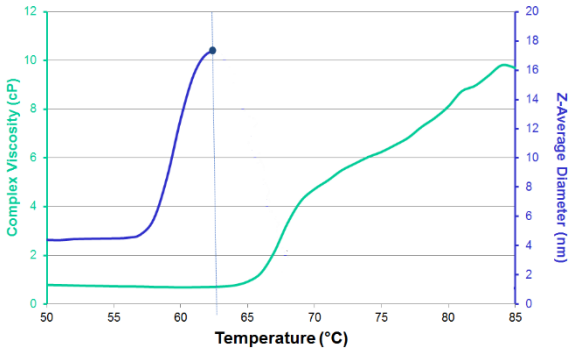

Figure 5. Complex viscosity from DLS-microrheology and Z-average diameter from DLS measurements as function of temperature.

Fig. 5 above indicates that there difference between increase in hydrodynamic size and bulk viscosity. The DLS-microrheology and Raman spectra can help understand the aggregation process of β-lactoglobulin as function of temperature. Fig. 6 shows the frequency spectrum at 50 and 68°C.

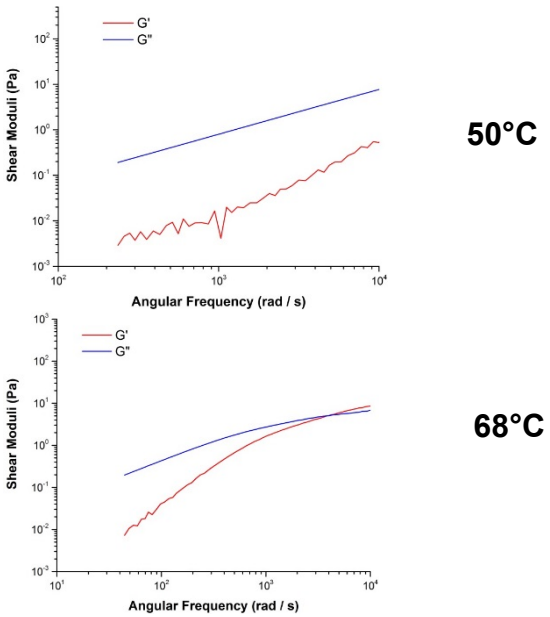

Figure 6. Frequency spectrum for β-lactoglobulin as function of temperature

Fig. 6 shows that at 50°C the protein solution is still in a dilute state but at 68°C the sample is approaching the rubbery plateau. Increased temperature shows similar behaviour but prolonged terminal relaxation times.

The Raman spectra intensity peak at 178 cm^{-1} and the normalized complex viscosity is shown in fig. 7.

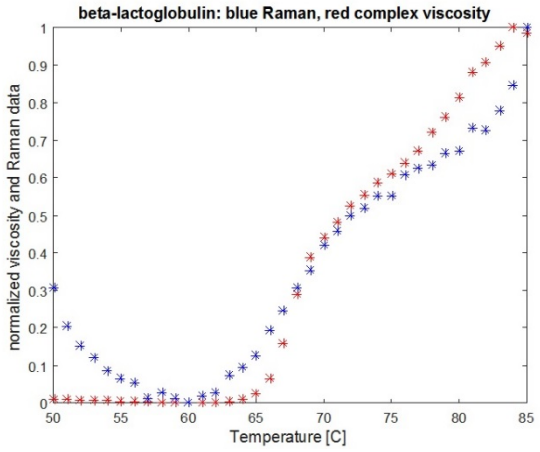

Figure 7. Normalized complex viscosity and Raman data at 178cm^{-1} vs. temperature

Fig. 7. Shows that Raman intensity peak at 178cm-1 has a minimum at 60°C indicating a change in the structure bounded water but that at higher temperatures the increased viscosity is clearly dependant on the increased structuring and confinement of water molecules.

Surfactant micelles (SLES & CapB)

Surfactant mixtures of the anionic sodium lauryl ether sulphate (SLES) and the zwitterionic cocoamidopropyl betaine forms elongated worm-like micelles in the presence of salt. Fig. 8 shows the zero shear viscosity and the relative Raman intensity at

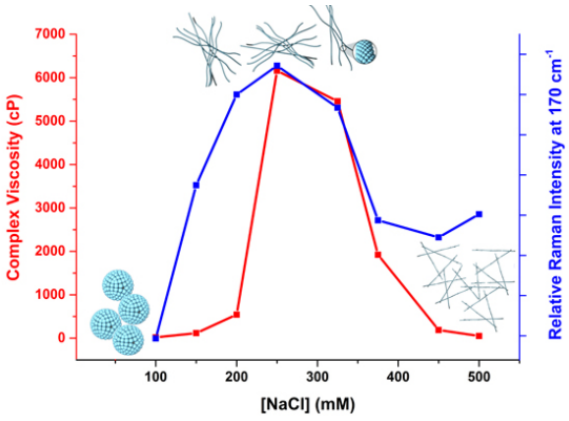

Figure 8. The zero shear viscosity and the relative Raman intensity at 170 cm^{-1} as function of salt concentration for a SLES:CapB mixture.

170 cm^{-1} curve for SLES/CAPB mixture (14:2 w/w %) at different salt concentrations determined using DLS-microrheology and Raman spectroscopy.

Fig. 8 shows a maximum in viscosity at 250mM NaCl that corresponds well with the samples viscoelastic character and that the increased viscosity corresponds with increased bound water. At higher concentrations the relative Raman intensity is different compared to before the viscosity maximum indicating a different extent of water confinement. At higher salt concentrations the relative Raman intensity is starting to increase while the viscosity becomes lower.

To further understand this increased relative intensity in bound water with increased concentration the basic correlogram for the different DLS measurements in fig. 9 are used.

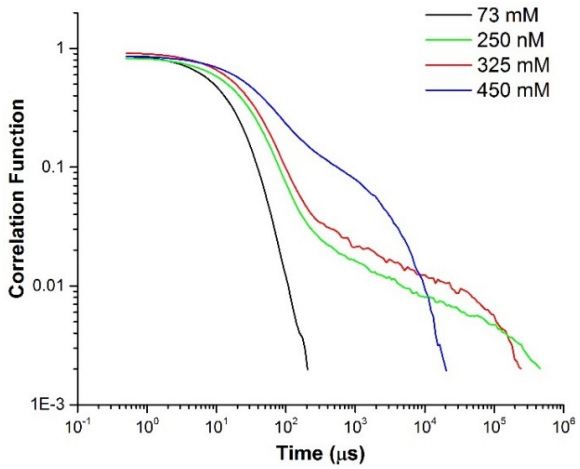

Figure 9. The correlation function (correlogram) vs. time at different salt concentrations

The correlogram show that the lowest salt concentration has a fast and single decay. Increasing salt concentration leads to longer decay times but also a slow mode is also detected as a shoulder in the correlation function. As salt concentration increases above the maximum viscosity concentration, the overall decay becomes faster and the slow mode is shifted towards shorter times. This can indicative of a microstructural change of the rodlike micelle structure.

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