

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Electronic Supplementary Information

Oriented Aggregation of Calcium Silicate Hydrates Platelets by the Use of Comb-like Copolymers

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

1 Viscoelastic properties of diluted C-S-H suspensions

Dynamic rheometry experiments were performed on a C-S-H suspension stabilized by Polymer 1. The suspension contains 1,7%^w of C-S-H and 0,4%^w of Polymer 1. The main features of dynamic mode rheometry are in detail explained in many textbooks^[1,2,3]. In our study, a controlled-stress rheometer Physica MCR301 marketed by Anton Paar combined with a classical couette geometry tool was used and the suspension was submitted to a strain sweep test with in order to estimate the viscoelastic domain. The stress τ applied to the suspension is sinusoidal:

$$\tau = \tau_0 \cdot \cos(\omega t) \quad (1)$$

where ω is the frequency, τ_0 the amplitude of the oscillation and t the time and the resulting strain γ is recorded:

$$\gamma = \gamma_0 \cdot \cos(\omega t + \delta) \quad (2)$$

where γ_0 is the amplitude of the strain and δ an angle. Most of the materials reveal a viscoelastic behavior, i.e. they exhibit a complex modulus G^* when they are submitted to a stress, the modulus being the function linking the stress and the strain:

$$G^*(\omega) = \frac{\tau}{\gamma} = G' + iG'' \quad (3)$$

where G' is the storage (elastic) modulus and G'' the loss (viscous) modulus. The frequency was 1 Hz. We observe in Fig. S1 that $G' > G''$ at low strain, that means that the solid-like behavior is predominant. From very low strain up to 1%, G' remains constant. This range defines the domain of linear viscoelasticity of the suspension where stress and strain are proportional via the modulus. The existence of such a domain is related to the formation of a coherent network of particles^[4,5,6]. Considering the very low volume concentration of particles, it can be concluded that the particles interact and are extremely connected. For this case, the critical strain is 1%, above this strain the network will be broken.

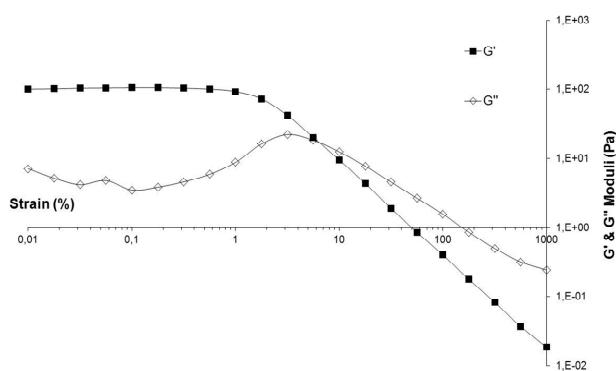


Fig. S1 Evolution of the elastic and viscous moduli against applied sinusoidal strain on a 1,7%^w C-S-H suspension containing 0,4% of Polymer 1.

2 SAXS fractal model

The spherically averaged scattering intensity of N particles per unit volume V can be written as follows:

$$I(q) = K \cdot F^2(q) \cdot S(q) \quad (4)$$

where K is a constant, F^2 is the form factor describing the shape and the size of the particles. The last term in the Eq. 4, the structure factor S, includes the scattering contributions due to correlations among the particles. It has to be mentioned that this is an approximation which is strictly valid only for monodisperse, spherically symmetric systems. Several approximations such as the local monodisperse approximation (local monodispersity), or the decoupling approximation (for slightly anisotropic particles) have been introduced in literature^[7]. For the sake of simplicity we use Eq. 4 in the following, although we are aware that none of these approximations might be strictly valid. Building a valid model consists of the right description of the structure and form factors. This will be the point of the following demonstration.

2.1 Form factor (thin disk like shape)

As the interpretation of scattering pattern of planar particles is the

objective of the present work, the scattering form factor of a particle with disk like shape will be described here. As compared to the very simple model described in appendices, the primary plate thickness is not neglected and the structure factor is described by a fractal cluster model with 3 parameters. We consider a thin disk with diameter D and thickness L, where $D \gg L$.

The form factor of randomly oriented thin disks can be shown to factorize into a form factor $P_1(q)$ for the shorter dimensions and a shape form factor $P_0(q)$ for the larger dimension^[8].

$$F_{disk}^2(q, \rho, L, D) = P_{disk}(q, \Delta\rho, L, D) = P_0(q, D) \cdot P_1(q, \Delta\rho, L) \quad (5)$$

The shape form factor $P_0(q)$ of an infinitely thin disk is:

$$P_0(q, D) = \frac{2\pi^2 \left(\frac{D}{2}\right)^4}{\left(q \left(\frac{D}{2}\right)\right)^2} \left(1 - \frac{J_1\left(2q \cdot \frac{D}{2}\right)}{q \cdot \frac{D}{2}} \right) \quad (6)$$

where J_1 is the Bessel function of the first order. A Gaussian distribution was used to describe the size distribution in the diameter of the plate centered in D. This normal distribution has the variance σ^2 , meaning that σ the width of the distribution is/can be also a fit parameter. Then the shape form factor is given by:

$$P_0(q) = \int_0^\infty \frac{2\pi^2 \left(\frac{D}{2}\right)^4}{\left(q \left(\frac{D}{2}\right)\right)^2} \left(1 - \frac{J_1\left(2q \cdot \frac{D}{2}\right)}{q \cdot \frac{D}{2}} \right) f(D) dD \quad (7)$$

where $f(D)$ is:

$$f(D) = \frac{N}{c_{Gauss}} e^{-\frac{(D-D_0)^2}{2\sigma^2}} \quad (8)$$

$$c_{Gauss} = \sqrt{\frac{\pi}{2}} \sigma \left(1 + \operatorname{erf} \left(\frac{D_0}{\sqrt{2}\sigma} \right) \right) \quad (9)$$

c_{Gauss} is chosen such that

$$\int_0^\infty f(D) dD = N \quad (10)$$

where N is number of the plates. The remaining factor P_1 , when squared and averaged, is related only to the thickness of the disk multiplied by the contrast and can be written as:

$$P_1(q, \Delta\rho, L) = \left((\Delta\rho)L \cdot \frac{\sin\left(\frac{qL}{2}\right)}{\frac{qL}{2}} \right)^2 \quad (11)$$

Therefore, the form factor of a thin disk can be written as:

$$P_{disk}(q, \Delta\rho, L, D) = K \cdot \left((\Delta\rho)L \cdot \frac{\sin\left(\frac{qL}{2}\right)}{\frac{qL}{2}} \right)^2 \cdot \int_0^\infty \frac{2\pi^2 \left(\frac{D}{2}\right)^4}{\left(q \left(\frac{D}{2}\right)\right)^2} \left(1 - \frac{J_1\left(2q \cdot \frac{D}{2}\right)}{q \cdot \frac{D}{2}} \right) f(D) dD \quad (12)$$

where the integral has to be calculated numerically during fitting.

2.2. Structure factor (mass fractal)

For mass fractal objects, it is well known that the scattered intensity $I(q)$ follows a power law, $I(q) \propto q^{-d}$, where d is the fractal dimension. In the case of mass fractals the fractal dimension varies as $1 < d \leq 3$.

The structure factor is adapted from Sorensen^[9,10], and is called the shape factor there (because it has to do with the shape of the aggregates). The structure factor used to describe the C-S-H clusters/ aggregates at low q , has a Gauss cut-off^[7,11] in the mass fractal model and can be represented by:

$$S_{Gauss}(q, \zeta, d, r_0) = 1 + \Gamma\left[\frac{d}{2}\right] \frac{d}{2} \left(\frac{\zeta}{r_0}\right)^d {}_1F_1\left[\frac{d}{2}, \frac{3}{2}, -\frac{q^2 \zeta^2}{8}\right] \quad (13)$$

where d is the fractal dimension, ζ is the cut-off length for the fractal correlations, $\Gamma(x)$ is the gamma function, r_0 is the distance characterizing the interaction between particles and ${}_1F_1[x]$ is the Kummer or hypergeometric function. The meaning of ζ is only qualitative and has to be made precise in any particular situation. Generally speaking, it represents the characteristic distance above which the mass distribution in the sample is no longer described by the fractal law. In practice, it may represent a measure for the size of an aggregate or more generally, a correlation length in a disordered material.

At the end, multi-structural features exist in the sample, a crossover from primary plate to fractal will be manifested in the SAXS profiles. In such cases, the scattered intensity can be fitted to the general equation:

$$I(q) = K \cdot \left[\left((\Delta\rho)L \cdot \frac{\sin\left(\frac{qL}{2}\right)}{\frac{qL}{2}} \right)^2 * \int_0^\infty \frac{2\pi^2 \left(\frac{D}{2}\right)^4}{\left(q \left(\frac{D}{2}\right)\right)^2} \left(1 - \frac{J_1\left(2q \cdot \frac{D}{2}\right)}{q \cdot \frac{D}{2}} \right) f(D) dD \right] * \left[1 + \Gamma\left[\frac{d}{2}\right] \frac{d}{2} \left(\frac{\zeta}{r_0}\right)^d {}_1F_1\left[\frac{d}{2}, \frac{3}{2}, -\frac{q^2 \zeta^2}{8}\right] \right] \quad (14)$$

Notes and references

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