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Microstructures and mechanical properties of dense particle gels: Microstructural characterisation

Iwan Schenker[a,*], Frank T. Filser[a],
Tomaso Aste[b], Ludwig J. Gauckler[a]

[a] Nonmetallic Materials, Department of Materials, ETH Zurich, Zurich CH-8093, Switzerland
[b] Department of Applied Mathematics, RSPhysSE, The Australian National University, 0200 Australia

Abstract

The macroscopic mechanical properties of wet ceramic green bodies and densely packed coagulated colloidal particle gels strongly depend on the local arrangement of the powder particles on length scales of a few particle diameters. Heterogeneous microstructures exhibit up to one order of magnitude higher elastic properties and yield strengths than their homogeneous counterparts. The microstructures of these gels are analysed by the "straight path" method quantifying quasi-linear arrangements of particles. They show similar characteristics than force chains bearing the mechanical load in granular material. Applying this concept to gels revealed that heterogeneous colloidal microstructures show a significantly higher straight path density and exhibit longer straight paths than their homogeneous counterparts.

Keywords: Suspensions; Mechanical properties; Structure and microstructure; Granular matter

1. Introduction

Mechanical properties of coagulated colloids are important in many technical areas. Sediments,[1] ceramic pastes and suspensions,[2] pharmaceutical formulations such as crèmes and emulsions[3] and some food[4] are examples for which it is desirable to control the mechanical properties.

Recently, an internal gelation method (DCC: Direct Coagulation Casting)[5,6] was developed to process electrostatically stabilized suspensions to ceramic green bodies. Thereby it was found that this method permits to control the microstructures of wet ceramic green bodies for solids contents ranging from 20 to 60 vol%. The method allows for an in situ, i.e. undisturbed, destabilization of the colloidal suspension by either changing the pH of the solution (ΔpH-method) resulting in a "homogeneous" microstructure or by increasing the ionic strength (ΔI-method) leading to a "heterogeneous" microstructure.[7]

Fig. 1 shows cryo-SEM pictures of both microstructures. The particles in the ΔpH-coagulated wet green body present a highly homogeneous microstructure whereas in the ΔI-system inhomogeneities on the length scale of a few particle diameters are observed.

This qualitative observation was quantified by the three-dimensional pair-correlation function calculated from stereo cryo-SEM images[7] and by in situ performed diffusing wave spectroscopy (DWS) experiments during destabilization.[8] The structural differences correspond to differences in the heterogeneity: the first peak of the pair-correlation function at $r/d = 1$ (r being the distance between the particles and d the particle diameter) is higher for the ΔI-system indicating locally denser regions with higher average coordination number. Also, local maxima are present in the pair-correlation function for the ΔI-system at $r/d \cong 1.4$ and $\cong 1.6$ corresponding to characteristic peaks in hexagonally packed particle arrangements. During ΔI-destabilization particle rearrangements lead to larger pores and thus to less homogeneous microstructures,[8] whereas during the ΔpH-destabilization the initially stabilized, liquid-like microstructure, is "frozen", which results in a more homogeneous microstructure.

Rheological and uniaxial compression experiments on wet destabilized green bodies obtained by DCC[9,10] showed that colloids with heterogeneous microstructures have significantly higher elastic modulii and yield strengths than their homogeneous counterparts. Measuring the dynamics of the colloids

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* Corresponding author. Tel.: +41 44 632 6061; fax: +41 44 632 1132.
E-mail address: iwan.schenker@mat.ethz.ch (I. Schenker).

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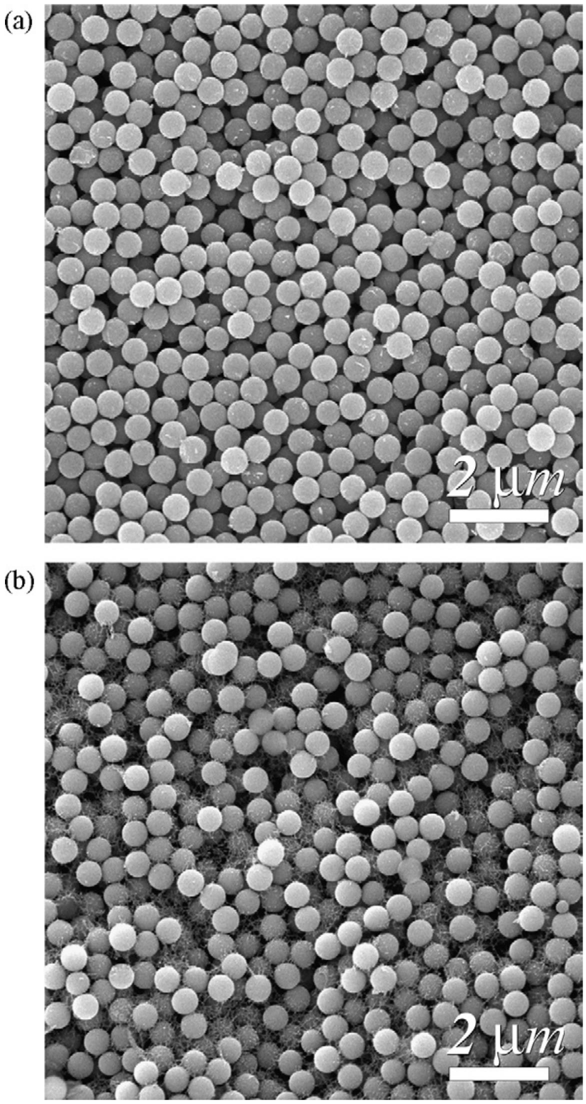

Fig. 1. Microstructure of coagulated silica suspensions at a solids loading of 40 vol% formed by the ΔpH- (a) and the ΔI-method (b) using the DCC process (particle diameter 525 nm). Micrographs obtained by cryo-SEM.[7]

during destabilization by DWS confirmed these findings quantitatively using a model for the storage modulus proposed by Krall and Weitz.[8,11]

Alkali-swellable polymers (ASP) were also used in order to introduce heterogeneities during the ΔpH-destabilization. Small amounts of 80 nm ASP particles were admixed to the powders under acidic conditions. These particles swell upon changing pH during the internal gelling reaction of the DCC process and enfold to 800 nm size producing less homogeneous microstructures. Those samples with swollen polymer particles showed much higher mechanical properties in comparison to samples without swellable polymers and hence more homogenous microstructures.[12] These samples present the same high mechanical properties as samples with heterogeneous microstructures produced by the ΔI-method.[12]

Examples of the rheologically measured elastic properties of mono-dispersed silica particle suspensions (particle diameter 200 nm) for different solids loadings destabilized by the ΔpH- and the ΔI-method, respectively, are shown in Fig. 2. Almost one order of magnitude higher elastic plateau storage modulii are measured for heterogeneous microstructures than for those with homogenous microstructures.[10]

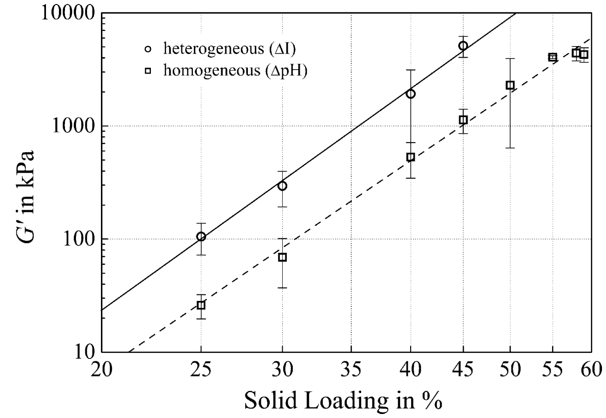

Fig. 2. Elastic plateau storage modulus G' of silica particle suspensions (particle diameter 200 nm) in dependence of the solids loading formed by the ΔpH- and the ΔI-method of the DCC process.[10]

In summary, strong evidence is given that the differences in macroscopic mechanical properties of coagulated particle suspensions are controlled by the differences in microstructure. An open question is now how these microstructural differences on particle length scales can have such a dramatic influence on the mechanical properties. Therefore, a concise quantitative analysis of microstructures of colloidal particle systems is needed.

In preceding works, various characterization methods, such as the radial pair-correlation function,[13] the bond angle distribution function,[13] the triangle distribution function[13] and the Minkowski functionals in conjunction with the parallel-body technique,[14] were applied to sets of microstructures generated by Brownian dynamics (BD) simulations.[15] These simulations were used to study the coagulation dynamics and the evolving microstructures in dense colloidal suspensions and the resulting microstructures agree well with experiments.[16]

While the pair-correlation function permits to quantify the amount of structural rearrangement during the coagulation,[13] the analysis using the Minkowski functionals in conjunction with the parallel-body technique supplies additional information on the structure's morphology resolving microstructural differences on a length scale limited by the largest pore size.[14] The bond angle distribution function and the triangle distribution functions are useful means to examine the local building blocks of the particle network.[13] Particular features, as for example, peaks in the respective distribution function have successfully been correlated to the structure's heterogeneity and porosity. The same conclusion is valid for the Minkowski functionals.[14]

All these four methods are good means to compare structures in terms of their heterogeneity. However, these structural descriptions do not unambiguously help to understand why more heterogeneous colloidal structures possess stronger mechanical properties as they do not adequately capture the microstructural characteristics that are responsible for the mechanical properties of these particle systems.